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Typical and Preferred Color Paper, Color Negative, and Color Reversal Photographic Elements and Processing

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I. Description of Typical Photographic Elements

This disclosure relates to components and embodiments useful for photographic materials.

Typically, the photographic materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a support to form part of a photographic element. Alternatively, they can be incorporated at a location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with development products such as oxidized color developing agent. Thus, as used herein, the term "associated" signifies that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable of reacting with silver halide development products.

To control the migration of various components, it may be desirable to include a high molecular weight hydrophobe or "ballast" group in the component molecule. Representative ballast groups include substituted or unsubstituted alkyl or aryl groups containing 8 to 40 carbon atoms. Representative substituents on such groups include alkyl, aryl, alkoxy, aryloxy, acyl, hydroxy, halogen, alkoxy, carbonyl, aryloxy, carbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido (also known as acylamino), carbamoyl, alkylsulfonoyl, arylsulfonoyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 40 carbon atoms. Such substituents can also be further substituted. Alternatively, the molecule can be made immobile by attachment to polymeric backbone.

It is understood throughout this research disclosure that any reference to a substituent by the identification of a group containing a substitutable hydrogen (e.g. alkyl, amine, aryl, alkoxy, heterocyclic, etc.), unless otherwise specifically stated, shall encompass not only the substituent's unsubstituted form, but also its form substituted with any photographically useful substituents. Usually the substituent will have less than 30 carbon atoms and typically less than 20 carbon atoms. Typical examples of substituents include alkyl, aryl, anilino, carbonamido, sulfonamido, alkylthio, arylthio, alkenyl, cycloalkyl, and further to these exemplified are halogen, cycloalkenyl, alkyl, heterocyclyl, sulfonoyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocyclyloxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxy, carbonylamino, aryloxy, carbonylamino, alkoxy, carbonyl, aryloxy, carbonyl, heterocyclylthio, spiro compound residues and bridged hydrocarbon compound residues.

The photographic elements can be single color elements or multicolor elements. Multicolor elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed

as a single segmented layer.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like.

In the following discussion of suitable materials for use in the emulsions and elements that can be used in conjunction with this photographic element, reference will be made to *Research Disclosure*, September 1994, Item 36544, published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ, England, which will be identified hereafter by the term "*Research Disclosure*." The contents of the *Research Disclosure*, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the *Research Disclosure*.

The silver halide emulsions employed in these photographic elements can be either negative-working or positive-working. Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I, and III-IV. Vehicles and vehicle related addenda are described in Section II. Dye image formers and modifiers are described in Section X. Various additives such as UV dyes, brighteners, luminescent dyes, antifogants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting agents are described, for example, in Sections VI-IX. Layers and layer arrangements, color negative and color positive features, scan facilitating features, supports, exposure and processing can be found in Sections XI-XX.

II. Couplers

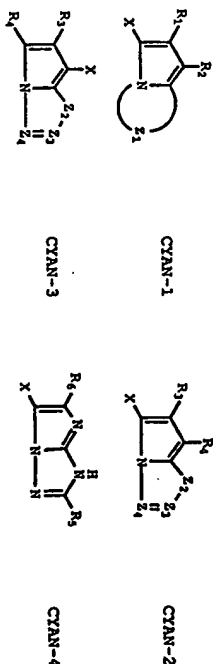
Couplers can be defined as being 4-equivalent or 2-equivalent depending on the the number of atoms of Ag⁺ required to form one molecule of dye. A 4-equivalent coupler can generally be converted into a 2-equivalent coupler by replacing a hydrogen at the coupling site with a different coupling-off group. Coupling-off groups are well known in the art. Such groups can modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, color correction and the like. Representative classes of such coupling-off groups include, for example, chloro, alkoxy, aryloxy, hetero-alkoxy, sulfonyloxy, acyloxy, acyl, heterocyclyl, sulfonamido, mercaptotetrazole, benzothiazole, alkylthio (such as

mercaptotripropionic acid), arylthio, phosphonyloxy and aryazo. These coupling-off groups are described in the art, for example, in U.S. Pat. Nos. 2,455,169; 3,227,551; 3,432,521; 3,476,563; 3,617,291; 3,880,661; 4,052,212 and 4,134,766; and in U.K. Patents 2,006,755A and 2,017,704A, the disclosures of which are incorporated herein by reference.

Image dye-forming couplers may be included in the element such as couplers that form cyan dyes upon reaction with oxidized color developing agents which are described in such representative patents and publications as: U.S. Pat. Nos. 2,367,531; 2,423,730; 2,474,293; 2,772,162; 2,895,826; 3,002,836; 3,034,892; 3,041,236; 4,883,746 and "Farbkuppler - Eine literatur Übersicht," published in *Agfa Mitteilungen*, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent. Also preferable are the cyan couplers described in, for instance, European Patent Application Nos. 544,322; 556,700; 556,777; 565,096; 570,006; and 574,948.

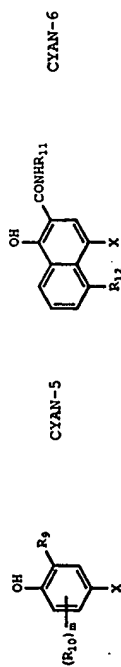
A. Cyan Couplers

Typical cyan couplers are represented by the following formulas:



wherein R₁, R₅ and R₈ each represent a hydrogen or a substituent; R₂ represents a substituent; R₃, R₄ and R₇ each represent an electron attractive group having a Hammett's substituent constant G_{para} of 0.2 or more and the sum of the G_{para} values of R₃ and R₄ is 0.65 or more; R₆ represents an electron attractive group having a Hammett's substituent constant G_{para} of 0.35 or more; X represents a hydrogen or a coupling-off group; Z₁ represents nonmetallic atoms necessary for forming a nitrogen-containing, six-membered, heterocyclic ring which has at least one dissociative group; Z₂ represents -C(R₇)= and -N=; and Z₃ and Z₄ each represent -C(R₈)= and -N=.

Even more preferable are cyan couplers of the following formulas:



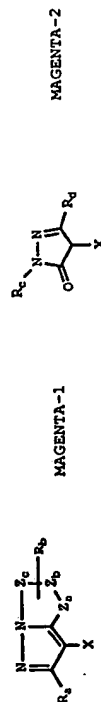
wherein R_9 represents a substituent (preferably a carbamoyl, ureido, or carbonamido group); R_{10} represents a substituent (preferably individually selected from halogens, alkyl, and carbonamido groups); R_{11} represents ballast substituent; R_2 represents a hydrogen or a substituent (preferably a carbonamido or sulphonamido group); X represents a hydrogen or a coupling-off group; and m is from 1-3.

A dissociative group has an acidic proton, e.g. $-NH-$, $-CH(R)-$, etc., that preferably has a pKa value of from 3 to 12 in water. Hammett's rule is an empirical rule proposed by I.P. Hammett in 1935 for the purpose of quantitatively discussing the influence of substituents on reactions or equilibria of a benzene derivative having the substituent thereon. This rule has become widely accepted. The values for Hammett's substituent constants can be found or measured as is described in the literature. For example, see C. Hansch and A.J. Leo, *J. Med. Chem.*, 16, 1207 (1973); *J. Med. Chem.*, 20, 304 (1977); and J.A. Dean, *Lange's Handbook of Chemistry*, 12th Ed. (1979) (McGraw-Hill).

Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,600,788; 2,369,489; 2,343,703; 2,311,082; 2,908,573; 3,062,653; 3,152,896; 3,519,429 and "Farbkuppler - Eine Literature Übersicht," published in *Agfa Mitteilungen*, Band III, pp. 126-156 (1961). Preferably such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents. Especially preferred couplers are 1H-pyrazolo [5,1-c]-1,2,4-triazole and 1H-pyrazolo [1,5-b]-1,2,4-triazole. Examples of 1H-pyrazolo [5,1-c]-1,2,4-triazole couplers are described in U.K. Patent Nos. 1,247,493; 1,252,418; 1,398,979; U.S. Patent Nos. 4,443,536; 4,514,490; 4,540,654; 4,590,153; 4,665,015; 4,822,730; 4,945,034; 5,017,465; and 5,023,170. Examples of 1H-pyrazolo [1,5-b]-1,2,4-triazoles can be found in European Patent applications 176,804; 177,765; U.S. Patent Nos. 4,659,652; 5,066,575; and 5,250,400.

B. Magenta Couplers

Typical pyrazolotriazole and pyrazolone couplers are represented by the following formulas:



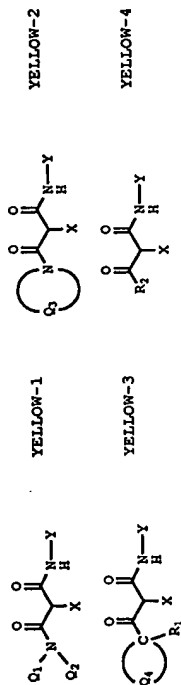
wherein R_a and R_b independently represent H or a substituent; R_c is

a substituent (preferably an aryl group); R_d is a substituent (preferably an anilino, carbonamido, ureido, carbamoyl, alkoxy, aryloxy, carbonyl, alkoxy, carbonyl, or N-heterocyclic group); X is hydrogen or a coupling-off group; and Z_a , Z_b , and Z_c are independently a substituted methine group, $=N-$, $=C-$, or $-NH-$, provided that one of either the Z_a-Z_b bond or the Z_b-Z_c bond is a double bond and the other is a single bond, and when the Z_b-Z_c bond is a carbon-carbon double bond, it may form part of an aromatic ring, and at least one of Z_a , Z_b , and Z_c represents a methine group connected to the group R_b .

C. Yellow Couplers

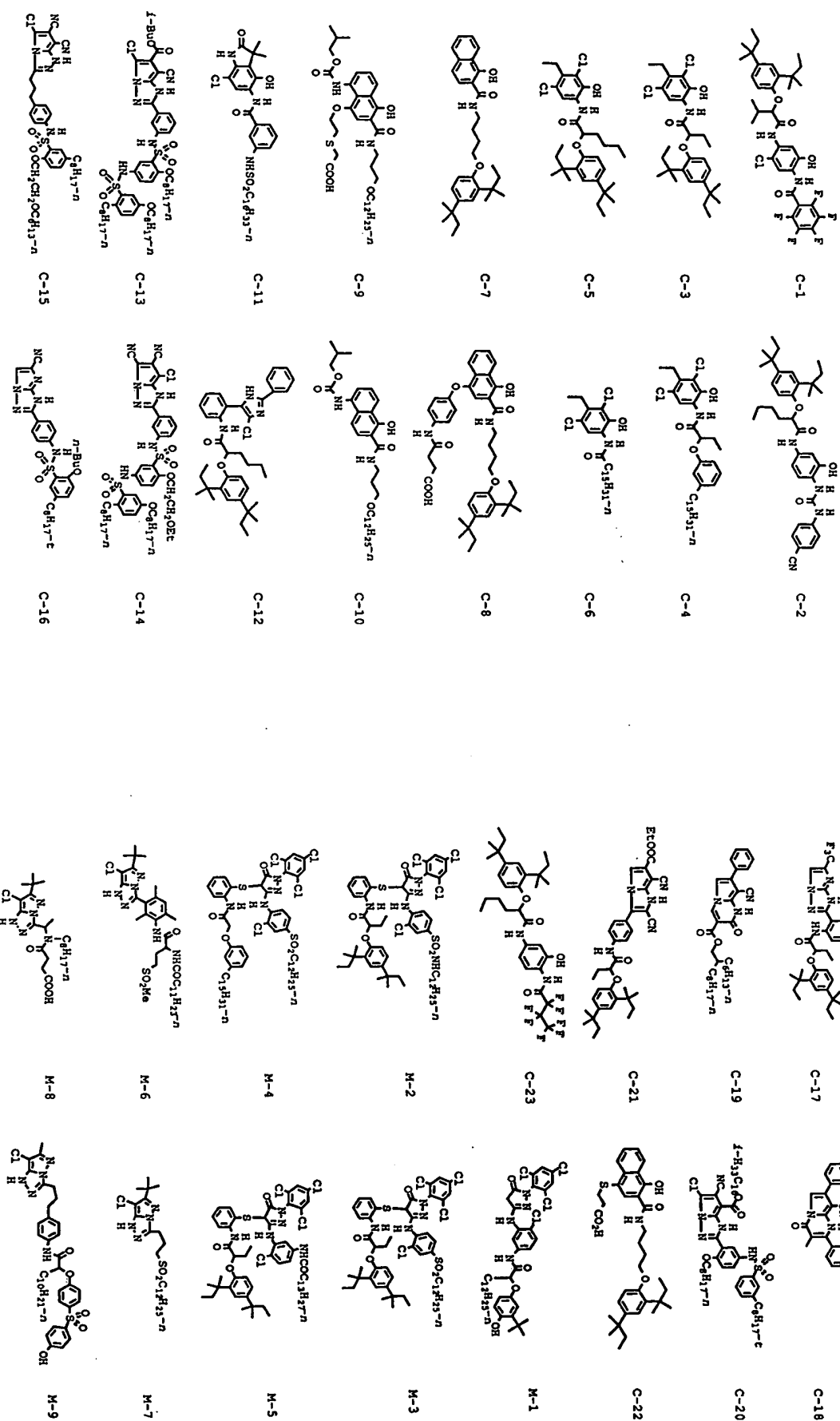
Couplers that form yellow dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Pat. Nos. 2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; 3,447,928 and "Farbkuppler - Eine Literature Übersicht," published in *Agfa Mitteilungen*, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds. Also preferred are yellow couplers such as described in, for example, European Patent Application Nos. 482,552; 510,535; 524,940; 543,367; and U.S. Patent No. 5,238,803. For improved color reproduction, couplers which give yellow dyes that cut off sharply on the long wavelength side are particularly preferred (for example, see U.S. Patent No. 5,360,713).

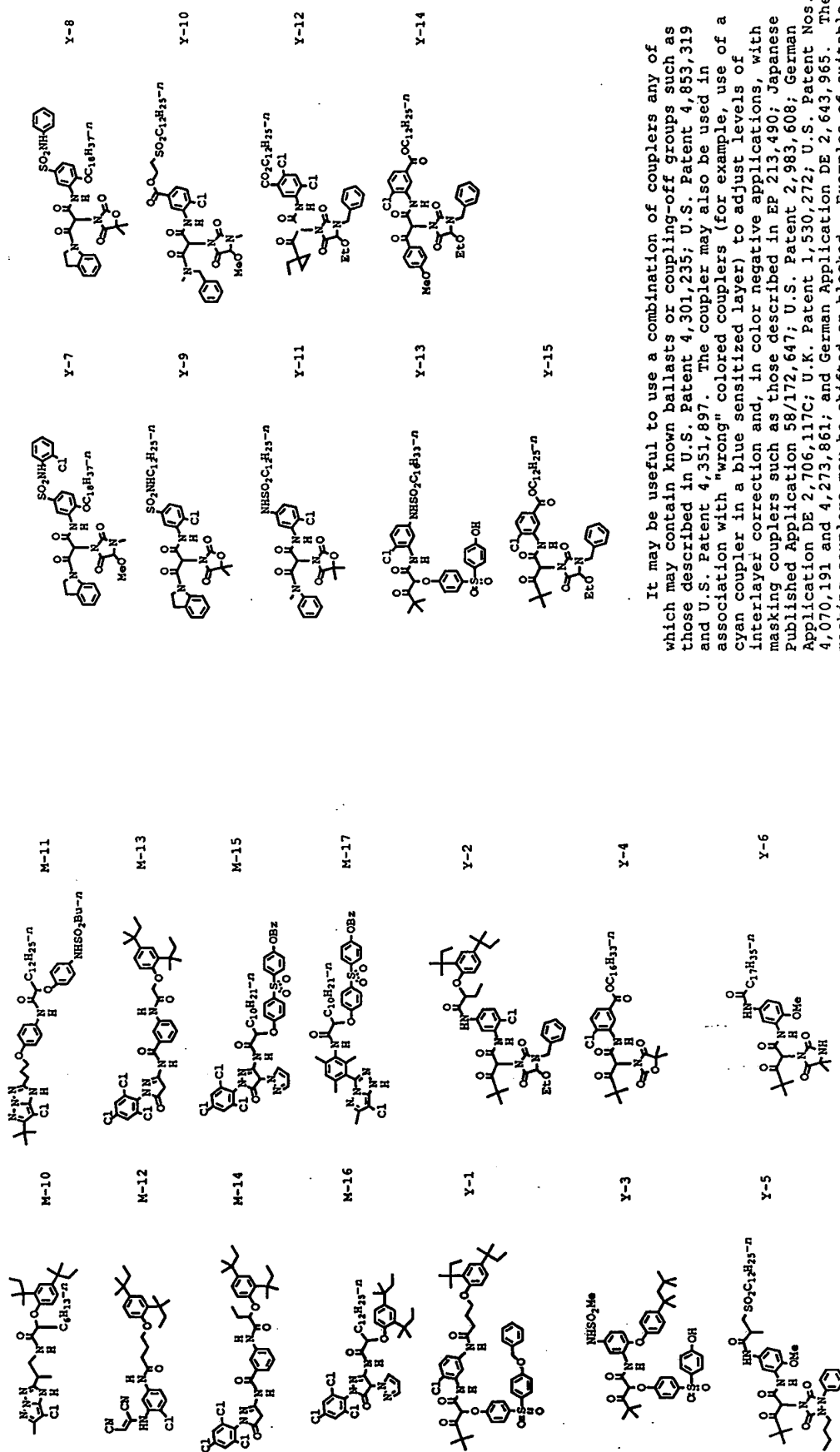
Typical preferred yellow couplers are represented by the following formulas:



wherein R_1 , R_2 , Q_1 and Q_2 each represent a substituent; X is hydrogen or a coupling-off group; Y represents an aryl group or a heterocyclic group; Q_3 represents an organic residue required to form a nitrogen-containing heterocyclic group together with the $>N-$; and Q_4 represents nonmetallic atoms necessary to form a 3- to 5-membered hydrocarbon ring or a 3- to 5-membered heterocyclic ring which contains at least one hetero atom selected from N, O, S, and P in the ring. Particularly preferred is when Q_1 and Q_2 each represent an alkyl group, an aryl group, or a heterocyclic group, and R_2 represents an aryl or tertiary alkyl group. Typical couplers that may be used with the photographic elements are shown below.

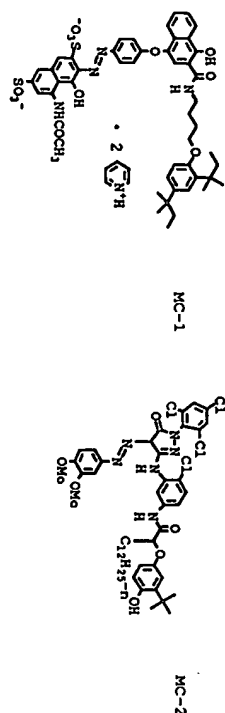
D. Structures of Typical Couplers





It may be useful to use a combination of couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent 4,301,235; U.S. Patent 4,853,319 and U.S. Patent 4,351,897. The coupler may also be used in association with "wrong" colored couplers (for example, use of a cyan coupler in a blue sensitized layer) to adjust levels of interlayer correction and, in color negative applications, with masking couplers such as those described in EP 213,490; Japanese Published Application 58/172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; U.S. Patent Nos. 4,070,191 and 4,273,861; and German Application DE 2,643,965. The masking couplers may be shifted or blocked. Examples of suitable masking couplers include, but are not limited to, the following.

E. Masking Couplers



III. BARCs, Nucleating Agents, ETAs, Antifoggants, Scavengers

The photographic element may contain materials that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784, may be useful. Also contemplated is use of the compositions in association with nucleating agents, development accelerators or their precursors (UK Patent 2,097,140 and U.K. Patent 2,131,188), electron transfer agents (U.S. 4,859,578 and U.S. 4,912,025), antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid, catechol, ascorbic acid, hydrazides (U.S. 4,923,787), sulfenamides, and non color-forming couplers. Further contemplated are the use of development accelerator releasing couplers (DARCs) as described in U.S. Patent Nos. 4,820,616; 4,948,712; 5,132,201; 5,213,942; and 5,221,600; EP 303,301; and EP 364,280.

IV. Color Fog Inhibitors

Suitable hydroquinone color fog inhibitors include, but are not limited to compounds disclosed in EP 69,070; EP 98,241; EP 265,808; Japanese Published Patent Applications 61/233,744; 62/118,250; and 62/178,257. In addition, specifically contemplated are 1,4-benzenediphenolic acid, 2,5-dihydroxy- Δ,Δ,Δ' -tetramethyl-, dihexyl ester; 1,4-benzenediphenolic acid, 2-hydroxy-5-methoxy- Δ,Δ,Δ' -tetramethyl-, dihexyl ester; and 2,5-dimethoxy- Δ,Δ,Δ' -tetramethyl-, dihexyl ester.

V. Discoloration Inhibitors

Various kinds of discoloration inhibitors can be used in conjunction with these photographic elements. Typical examples of organic discoloration inhibitors include hindered phenols represented by hydroquinones, 6-hydroxychromans, 5-hydroxy-coumarins, spirochromans, *p*-alkoxyphenols and bisphenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines, and ether or ester derivatives obtained by silylation, alkylation or acylation of phenolic hydroxy groups of the above compounds. Also, metal complex salts represented by (bis-salicylaldoximate)nickel complex and (bis-*N,N*-dialkylidithio-carbamate)nickel complex can be employed as a discoloration

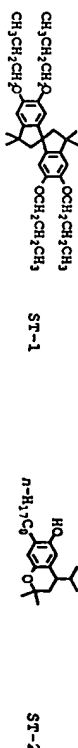
inhibitor. Specific examples of the organic discoloration inhibitors are described below. For instance, those of hydroquinones are disclosed in U.S. 2,360,290, 2,418,613, 2,700,453, 2,701,197, 2,710,801, 2,816,028, 2,728,659, 2,732,300, 2,735,765, 3,982,944 and 4,430,425, and British Patent 1,363,921, and so on; 6-hydroxychromans, 5-hydroxycoumarins, spirochromans are disclosed in U.S. 3,432,300, 3,573,050, 3,574,627, 3,698,909 and 3,764,337, and Japanese Published Patent Application 52/152,225, and so on; spiroindanes are disclosed in U.S. 4,360,589; those of *p*-alkoxyphenols are disclosed in U.S. 2,735,765, British Patent 2,066,975, Japanese Published Patent Applications 59/010,539 and 57/019,765, and so on; hindered phenols are disclosed, for example, in U.S. 3,700,455, 4,228,235, Japanese Published Patent Applications 52/072,224 and 52/006,623, and so on; gallic acid derivatives, methylenedioxybenzenes and aminophenols are disclosed in U.S. 3,457,079, 4,332,886, and Japanese Published Patent Application 56/021,144, respectively; hindered amines are disclosed in U.S. 3,336,135, 4,268,593, British Patents 1,326,889, 1,354,313 and 1,410,846, Japanese Published Patent Applications 51/001,420, 58/114,036, 59/053,846, 59/078,344, and so on; those of ether or ester derivatives of phenolic hydroxy groups are disclosed in U.S. 4,155,765, 4,174,220, 4,254,216, 4,279,990, Japanese Published Patent Applications 54/145,530, 55/006,321, 58/105,147, 59/010,539, 57/037,856, 53/003,263 and so on; and those of metal complexes are disclosed in U.S. 4,050,938, 4,241,155, 4,346,165, 4,540,653 and 4,906,559.

VI. Polymeric Addenda

Various types of polymeric addenda could be advantageously used in conjunction with the photographic element. Recent patents, particularly relating to color paper, have described the use of oil-soluble water-insoluble polymers in coupler dispersions to give improved image stability to light, heat and humidity, as well as other advantages, including abrasion resistance, and manufacturability of product. These are described, for instance, in EP 324,476, U.S. Patent Nos. 4,857,449, 5,006,453, and 5,055,386. In a preferred embodiment, a yellow or cyan image coupler, permanent solvent, and a vinyl polymer with a high glass transition temperature and moderate molecular weight (ca. 40,000) are dissolved together with ethyl acetate, the solution is emulsified in an aqueous solution containing gelatin and surfactant to give fine particles, and the ethyl acetate is removed by evaporation. Preferred polymers include poly(*N*-t-butylacrylamide) and poly(methyl methacrylate).

Stabilizers and scavengers that can be used in these photographic elements, but are not limited to, the following.

VII. Structures of Stabilizers and Scavengers



limited to poly(vinyl alcohol), partially hydrolyzed poly(vinylacetate/ vinylalcohol), hydroxyethyl cellulose, poly(acrylic acid), poly(1-vinylpyrrolidone), poly(sodium styrene sulfonate), poly(2-acrylamido-2-methane sulfonic acid), and polyacrylamide. Copolymers of these polymers with hydrophobic monomers may also be used.

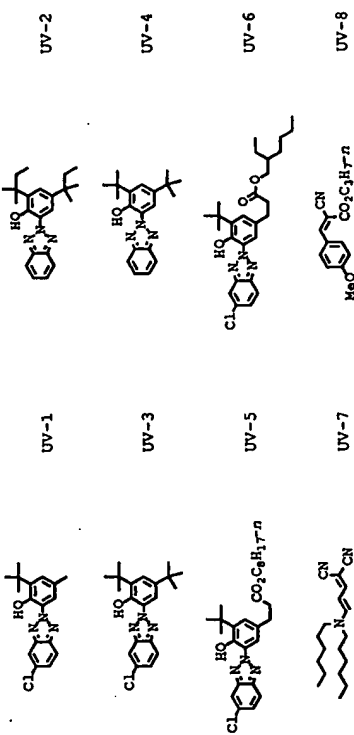
Photographically useful compounds may be dissolved in high-boiling or permanent solvents. Optionally, auxiliary solvents may be used to assist dissolution of the photographically useful compound in the permanent solvent. The auxiliary solvent, if present, is then removed by evaporation, washing or dialysis. Examples of solvents which may be used include the following.

IX. Solvents

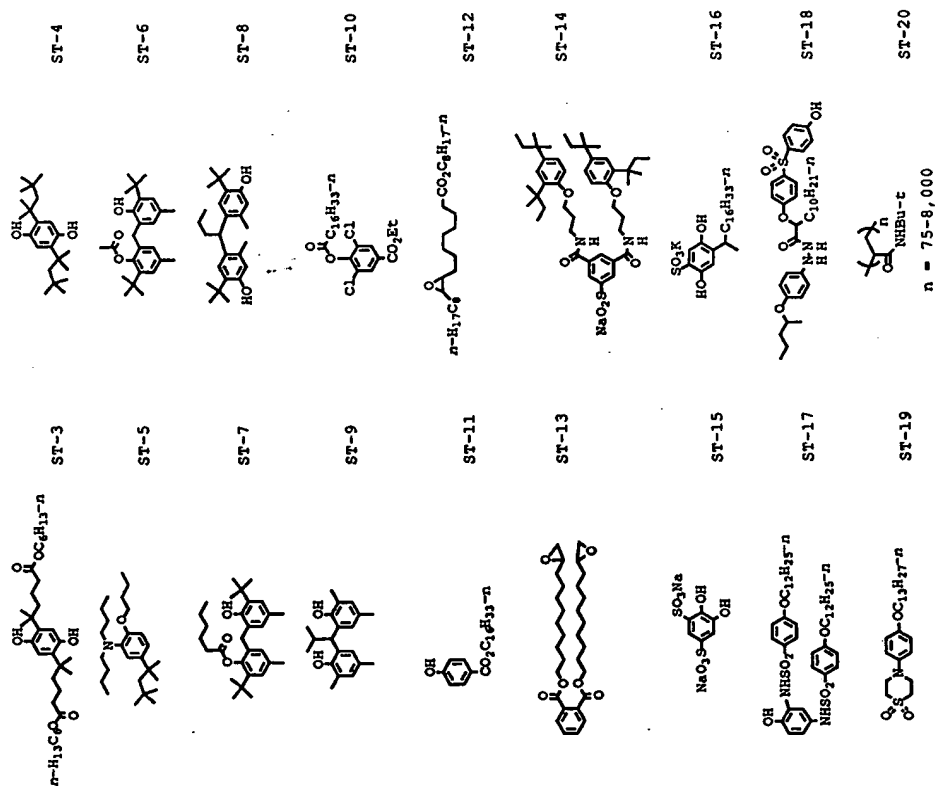
Tributyl phosphate	S-1
Dibutyl phthalate	S-2
N,N-Diethyldodecanamide	S-3
N,N-Dibutyldodecanamide	S-4
Tris(2-ethylhexyl)phosphate	S-5
Acetyl tributyl citrate	S-6
2,4-Di-tert-pentylphenol	S-7
2-(2-Butoxyethoxy)ethyl acetate	S-8
1,4-Cyclohexyldimethylene Bis(2-ethylhexanoate)	S-9

The dispersions used in photographic elements may also include ultraviolet (UV) stabilizers and so called liquid UV stabilizers such as described in U.S. Patent Nos. 4,992,358; 4,975,360; and 4,587,346. Examples of UV stabilizers are shown below.

X. UV Stabilizers



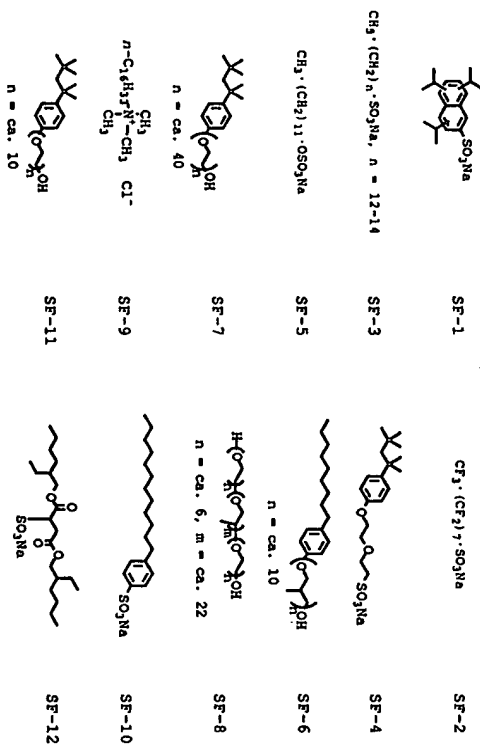
The aqueous phase may include surfactants. Surfactant may be cationic, anionic, zwitterionic or non-ionic. Useful surfactants include, but are not limited to the following.



VIII. Dispersions

The aqueous phase of the dispersions of the photographic elements may comprise a hydrophilic colloid. This may be gelatin or a modified gelatin such as acetylated gelatin, phthalated gelatin, oxidized gelatin, etc. The hydrophilic colloid may be another water-soluble polymer or copolymer including, but not

XI. Surfactants



Further, it is contemplated to stabilize photographic dispersions prone to particulate growth through the use of hydrophobic, photographically inert compounds such as disclosed by Zengerle et al in USSN 07/978,104.

XII. Hardeners

Various types of hardeners can be used in the photographic element. In particular, bis(vinylsulphonyl) methane, bis(vinylsulphonyl) methyl ether, 1,2-bis(vinylsulphonyl-acetamido) ethane, 2,4-dichloro-6-hydroxy-s-triazine, triacryloyltriazine, and pyridinium, 1-(4-morpholinylcarbonyl)-4-(2-sulfoethyl)-, inner salt are particularly useful. Also useful are so-called fast acting hardeners as disclosed in U.S. Pat. Nos. 4,418,142, 4,618,573, 4,673,632, 4,863,841, 4,877,724, 5,009,990, 5,236,822.

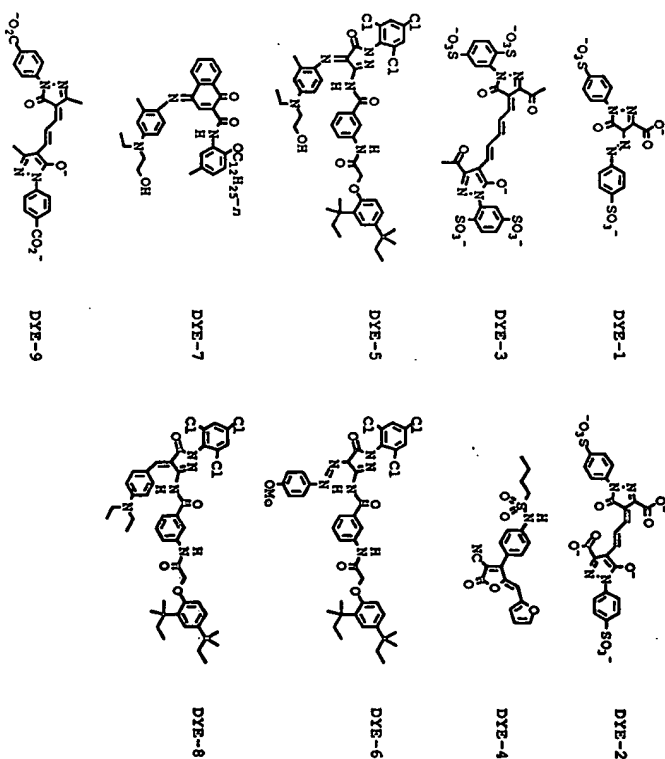
XIII. Filter and Absorber Dyes

The photographic elements may also contain filter dye layers comprising colloidal silver sol or yellow, cyan, and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Useful examples of absorbing materials are discussed in *Research Disclosure*, September 1994, Item 36544, Section VIII.

The photographic elements may also contain light absorbing materials that can increase sharpness and be used to control speed and minimum density. Examples of useful absorber dyes are described in U.S. 4,877,721, U.S. 5,001,043, U.S. 5,153,108, and U.S. 5,035,985. Solid particle dispersion dyes are described in U.S. Patent Nos. 4,803,150; 4,855,221; 4,857,446; 4,900,652; 4,900,653; 4,940,654; 4,948,717; 4,948,718; 4,950,586; 4,988,611;

4,994,356; 5,098,820; 5,213,956; 5,260,179; 5,266,454. Useful dyes include, but are not limited to, the following.

Dyes



Additionally, the photographic elements may contain "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 96,570; U.S. 4,420,556; and U.S. 4,543,323). Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

XIV. DIR(A)Rs

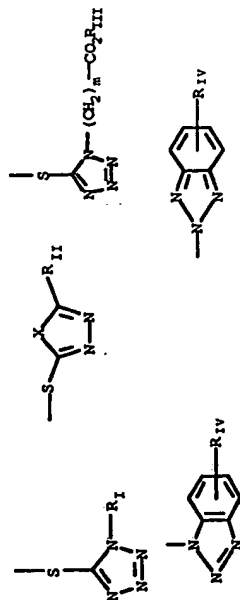
The photographic element may further contain image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIR's). Useful DIR compositions are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,146,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816;

4,607,004; 4,618,571; 4,678,739; 4,746,500; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,083; DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346,899; 362,870; 365,252; 365,345; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thittle and P.W. Vittum in *Photographic Science and Engineering*, Vol. 13, p. 174 (1969), incorporated herein by reference.

Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiaziazoles, benzotriazoles, tetrazoles, benzimidazoles, indazoles, isindazoles, mercaptotetrazoles, selenotetrazoles, mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, selenobenzimidazoles, benzodiazoles, mercaptooxazoles, mercaptothiadiazoles, mercaptodiazoles, mercaptotriazoles, mercaptooxadiazoles, mercaptodiazoles, mercaptotetrazoles, tellurotetrazoles or benzisodiazoles.

In a preferred embodiment, the inhibitor moiety or group is selected from the following formulas:



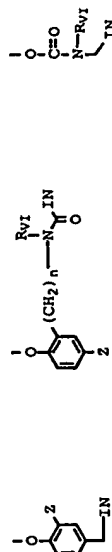
wherein R_I is selected from the group consisting of straight and branched alkyls of from 1 to about 8 carbon atoms, benzyl, phenyl, and alkoxy groups and such groups containing none, one or more than one such substituent; R_{II} is selected from R_I and -SR_I; R_{III} is a straight or branched alkyl group of from 1 to about 5 carbon atoms and m is from 1 to 3; R_{IV} is selected from the group consisting of hydrogen, halogens and alkoxy, phenyl and carbonamido groups, -COOR_V and -NHCOOR_V wherein R_V is selected from substituted and unsubstituted alkyl and aryl groups; and X is

selected from O, S, or N.

Although it is typical that the coupler moiety included in the developer inhibitor-releasing coupler forms an image dye corresponding to the layer in which it is located, it may also form a different color as one associated with a different film layer. It may also be useful that the coupler moiety included in the developer inhibitor-releasing coupler forms colorless products and/or products that wash out of the photographic material during processing (so-called "universal" couplers).

A. Timing Groups for DI(A)Rs

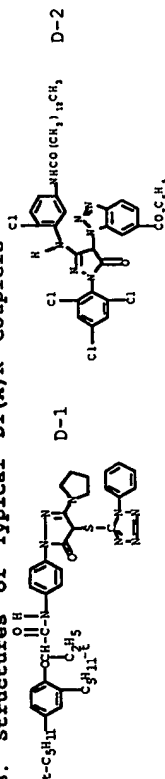
As mentioned, the developer inhibitor-releasing coupler may include a timing group which produces the time-delayed release of the inhibitor group such as groups utilizing the cleavage reaction of a hemiacetal (U.S. 4,146,396, Japanese Applications 60/249148; 60/249149); groups using an intramolecular nucleophilic substitution reaction (U.S. 4,248,962); groups utilizing an electron transfer reaction along a conjugated system (U.S. 4,409,323; 4,421,845; Japanese Applications 57/188035; 58/98728; 58/209736; 58/209738) groups utilizing ester hydrolysis (German Patent Application (OLS) No. 2,626,315); groups utilizing the cleavage of imino ketals (U.S. 4,546,073); groups that function as a coupler or reducing agent after the coupler reaction (U.S. 4,438,193; U.S. 4,618,571) and groups that combine the features described above. Typical timing groups or moieties have the following formulas:

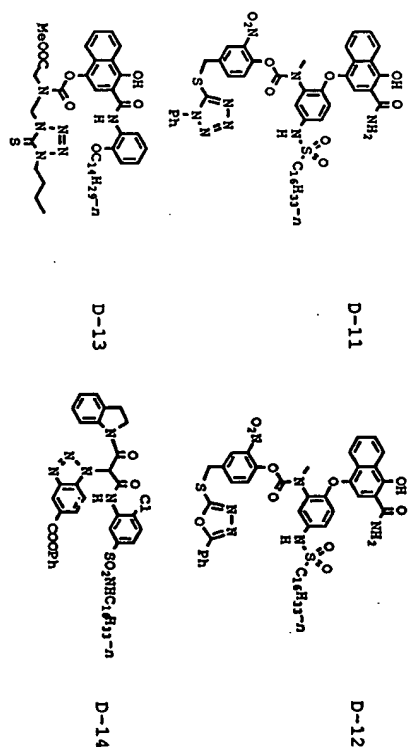
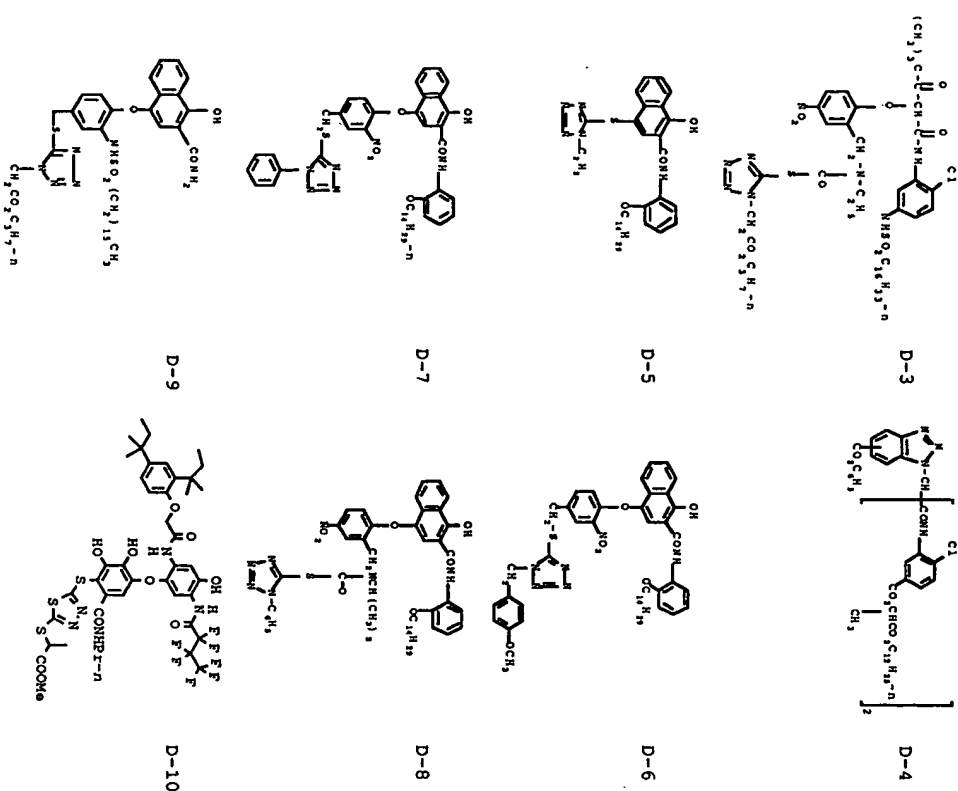


wherein IN is the inhibitor moiety, Z is selected from the group consisting of nitro, cyano, alkylsulfonyl, sulfamoyl (-SO₂NR₂); and sulfonamido (-NRSO₂R) groups; n is 0 or 1; and R_V is selected from the group consisting of substituted and unsubstituted alkyl and phenyl groups. The oxygen atom of each timing group is bonded to the coupling-off position of the respective coupler moiety of the DIAR.

Suitable developer inhibitor-releasing couplers for use in the present photographic element include, but are not limited to, the following.

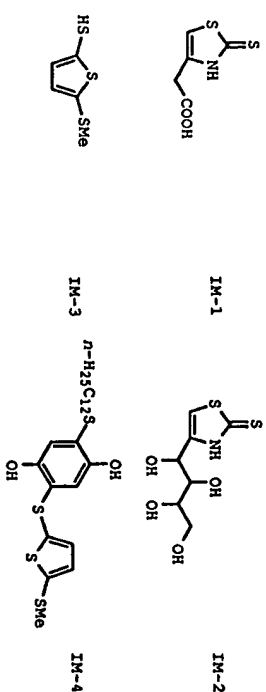
B. Structures of Typical DI(A)R Couplers

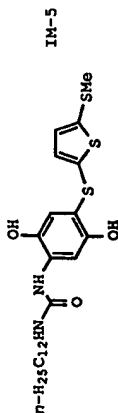




C. Image Modifiers for Color Reversal Films

Reversal films use two silver development steps during processing. The first is a non-chromogenic development or black and white development in which image modification can be achieved by iodide diffusion and inhibition of solution physical development. The iodide source is the silver halide grains which typically are 1 to 20 μ iodide. Iodide ion is released from the silver halide grains as a function of exposure and development and can reduce or inhibit solution physical development in surrounding silver halide layers thus providing a mechanism for interimage effects between layers, or increased acutance in the same layer. Organic compounds which enhance the inhibiting iodide effect can be incorporated into the imaging records or surrounding layers directly, or they can be released in an image-wise or non-image-wise fashion from other compounds. Examples of these compounds are shown below.





Sources of silver halide such as chemically fogged silver halide or solvents which increase the amount of silver in solution can increase the image modifying effect from iodide. Suppression of fog allows for interimage effects when there is no exposure in a record.

The second development step for reversal films is a chromogenic step in which image couplers either incorporated in the film or different color developer solutions form dyes as a result of reaction with phenylenediamines which have been oxidized by the remaining silver halide not developed in the first development step. Compounds which release silver development inhibitors as a function of dye formation (e.g. DI(A)R couplers) can be used to provide interlayer interimage and acutance effects. The most useful image modifying compounds for reversal are those that are more reactive toward oxidized developer than the image coupler of the layer in which they are incorporated or adjacent and which contain timing groups for delayed release of the inhibitor fragments. In order to create image modification from a inhibitor releasing compound the silver development must stop short of completion.

This can be accomplished by the amount of silver halide used and the amount and type of image modifying compound. It is useful for the image modifying compounds to release inhibitors which can restrain silver development as well as the inhibitor phenylmercaptotetrazole does.

Tools which can be used alone or in combination for obtaining better color reproduction of reversal films include: 1. Spectral sensitizing dyes which promote accurate spectral sensitivity to the silver halide grains of their respective color record. 2. Filter dyes or light filtering silver (e.g. Carey Lea silver) used in interlayer layers. 3. Image couplers that give yellow, magenta and cyan dyes which have minimum overlap of absorptions. 4. Image modifiers for the first development to enhance the iodide inhibition of solution physical development. 5. DI(A)R couplers for the second development to inhibit silver development as a function of dye formation such as D-6, D-7, D-8, D-10, D-11, and D-12. 6. Chemically or light fogged silver halide grains and solvents which enhance solution physical development. 7. Magenta image couplers that can enhance the inhibitor of DI(A)R couplers during color development such as D-1, M-6, M-7, M-8, and M-10.

xv. Emulsions

The emulsions can be surface-sensitive emulsions, i.e., emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-

sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

Any silver halide combination can be used for the photographic element, such as silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide, silver bromiodide, or silver chloriodide. In cases where the emulsion composition is a mixed halide, the minor component may be added in the crystal formation or after formation as part of the sensitization or melting. The shape of the silver halide emulsion grain can be cubic, pseudo-cubic, octahedral, tetradecahedral or tabular. The emulsions may be precipitated in any suitable environment such as a ripening environment, a reducing environment or an oxidizing environment.

Specific references relating to the preparation of emulsions of differing halide ratios and morphologies are Evans U.S. Patent 3,618,622; Atwell U.S. Patent 4,269,927; Wey U.S. Patent 4,414,306; Maskasky U.S. Patent 4,400,463; Maskasky U.S. Patent 4,713,323; Tufano et al U.S. Patent 4,804,621; Takada et al U.S. Patent 4,738,398; Nishikawa et al U.S. Patent 4,952,491; Ishiguro et al U.S. Patent 4,933,508; Hasebe et al U.S. Patent 4,820,624; Maskasky U.S. Patent 5,264,337; 5,275,930; and House et al U.S. Patent 5,320,938.

Emulsion precipitation is conducted in the presence of silver ions, halide ions and in an aqueous dispersing medium including, at least during grain growth, a peptizer. Grain structure and properties can be selected by control of precipitation temperatures, pH and the relative proportions of silver and halide ions in the dispersing medium. To avoid fog, precipitation is customarily conducted on the halide side of the equivalence point (the point at which silver and halide ion activities are equal). Manipulations of these basic parameters are illustrated by the citations including emulsion precipitation descriptions and are further illustrated by Matsuzaka et al U.S. Patent 4,497,895; Yagi et al U.S. Patent 4,728,603; Sugimoto U.S. Patent 4,755,456; Kishita et al U.S. Patent 4,847,190; Joly et al U.S. Patent 5,017,468; Wu U.S. Patent 5,166,045; Shibayama et al EPO 0 328 042, and Kawai EPO 0 531 799.

Reducing agents present in the dispersing medium during precipitation can be employed to increase the sensitivity of the grains, as illustrated by Takada et al U.S. Patent 5,061,614, Takada U.S. Patent 5,079,138 and EPO 0 434 012. Inoue U.S. Patent 5,185,241, Yamashita et al EPO 0 369 491, Ohashi et al EPO 0 371 338, Katsumi EPO 435 270 and 0 435 355 and Shibayama EPO 0 438 791. Conversely, oxidizing agents may be present during precipitation, used as a pretreatment of the dispersing medium (gelatin) or added to the emulsion after grain formation before or during sensitization, in order to improve the sensitivity/fog position of the silver halide emulsion or minimize residual ripening agent as illustrated by Komatsu et al JP 56-167393 and JP 59-195232, Mifune et al EPA 144 990 and EPA 166 347. Chemically sensitized core grains can serve as hosts for the precipitation of

shells, as illustrated by Porter et al U.S. Patents 3,206,313 and 3,327,322, Evans U.S. Patent 3,761,276, Atwell et al U.S. Patent 4,035,185 and Evans et al U.S. Patent 4,504,570.

A. Tabular Grain Emulsions

Especially useful for use with this photographic element are tabular grain silver halide emulsions. Specifically contemplated tabular grain emulsions are those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 micron (0.5 micron for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as $T = ECD/t^2$ where ECD is the average equivalent circular diameter of the tabular grains in microns and t is the average thickness in microns of the tabular grains.

The average useful ECD of photographic emulsions can range up to about 10 microns, although in practice emulsion ECD's seldom exceed about 4 microns. Since both photographic speed and granularity increase with increasing ECD's, it is generally preferred to employ the smallest tabular grain ECD's compatible with achieving aim speed requirements.

Emulsion tabularity increases markedly with reductions in tabular grain thickness. It is generally preferred that aim tabular grain projected areas be satisfied by thin ($t < 0.2$ micron) tabular grains. To achieve the lowest levels of grainularity it is preferred that aim tabular grain projected areas be satisfied with ultrathin ($t < 0.06$ micron) tabular grains. Tabular grain thicknesses typically range down to about 0.02 micron. However, still lower tabular grain thicknesses are contemplated. For example, Daubendiek et al U.S. Patent 4,672,027 reports a 3 mole percent iodide tabular grain silver bromodiodide emulsion having a grain thickness of 0.017 micron. Ultrathin tabular grain high chloride emulsions are disclosed by Maskasky in U.S. 5,217,858.

As noted above tabular grains of less than the specified thickness account for at least 50 percent of the total grain projected area of the emulsion. To maximize the advantages of high tabularity it is generally preferred that tabular grains satisfying the stated thickness criterion account for the highest conveniently attainable percentage of the total grain projected area of the emulsion. For example, in preferred emulsions,

tabular grains satisfying the stated thickness criteria above account for at least 70 percent of the total grain projected area. In the highest performance tabular grain emulsions, tabular grains satisfying the thickness criteria above account for at least 90 percent of total grain projected area.

Suitable tabular grain emulsions can be selected from among a variety of conventional teachings, such as those of the following: Research Disclosure, January 1983 Item 22534; U.S. Patent Nos. 4,339,520; 4,414,310; 4,433,048; 4,643,966; 4,647,528; 4,665,012; 4,672,027; 4,678,745; 4,693,964; 4,713,320; 4,722,886; 4,755,456; 4,775,617; 4,797,354; 4,801,522; 4,806,461; 4,835,095; 4,853,322; 4,914,014; 4,962,015; 4,985,350; 5,061,069 and 5,061,616. In

addition, use of [100] silver chloride emulsions as described in U.S. Patent 5,320,938 are specifically contemplated.

B. Emulsion Dopants

Dopants (any grain occlusions other than silver and halide ions) can be employed to modify grain structure and properties. Periods 3-7 ions, including Group VIII metal ions (Fe, Co, Ni and platinum metals (pm) Ru, Rh, Pd, Re, Os, Ir and Pt), Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Cu, Zn, Ga, As, Se, Sr, Y, Mo, Zr, Nb, Cd, In, Sn, Sb, Ba, La, W, Au, Hg, Tl, Pb, Bi, Ce and U can be introduced during precipitation. The dopants can be employed (a) to increase the sensitivity of either (a1) direct positive or (a2) negative working emulsions, (b) to reduce (b1) high or (b2) low intensity reciprocity failure, (c) to (c1) increase, (c2) decrease or (c3) reduce the variation of contrast, (d) to reduce pressure sensitivity, (e) to decrease dye desensitization, (f) to increase stability, (g) to reduce minimum density, (h) to increase maximum density, (i) to improve room light handling and (j) to enhance latent image formation in response to shorter wavelength (e.g. X-ray or gamma radiation) exposures. For some uses any polyvalent metal ion (pym) is effective. The selection of the host grain and the dopant, including its concentration and, for some uses, its location within the host grain and/or its valence can be varied to achieve aim photographic properties, as illustrated by B. H. Carroll, "Iridium Sensitization: A Literature Review", Photographic Science and Engineering, Vol. 24, No. 6 Nov./Dec. 1980, pp. 265267; Hochstetler U.S. Patent 1,951,933 (Cu); De Wilt U.S. Patent 2,628,167; Mueller et al U.S. Patent 2,950,972; Spence et al U.S. Patent 3,687,676 and Gilman et al U.S. Patent 3,761,267; Okubu et al U.S. Patent 3,890,154; Itasca et al U.S. Patent 3,901,711; Haby et al U.S. Patent 4,173,483; Atwell U.S. Patent 4,269,927; Weyde U.S. Patent 4,413,055; Akimura et al U.S. Patent 4,452,882; Menjo et al U.S. Patent 4,477,561; Haby et al U.S. Patent 4,581,327; Kobuta et al U.S. Patent 4,643,965; Yamashita et al U.S. Patent 4,806,462; Grzeskowiak et al U.S. Patent 4,828,962; Janusonis U.S. Patent 4,835,093; Leubner et al U.S. Patent 4,902,611; Inoue et al U.S. Patent 4,981,780; Kim U.S. Patent 4,997,751; Kawai et al U.S. Patent 5,057,402; Mekawa et al U.S. Patent 5,134,060; Kawai et al U.S. Patent 5,164,292; Asami U.S. Patents 5,166,044 and 5,204,234; Wu U.S. Patent 5,166,045; Yoshida et al U.S. Patent 5,229,263; Marchetti et al U.S. Patents 5,264,336 and 5,268,264; Komarita et al EPO 0 244 184; Miyoshi et al EPO 0 488 737 and 0 488 601; Ihama et al EPO 0 368 304; Tashiro EPO 0 405 938; Murakami et al EPO 0 509 674; Budz WO 93/02390; Okubo et al U.S. Patent 3,672,901; Yamasue et al U.S. Patent 3,901,713; and Miyoshi et al EPO 0 488 737.

When dopant metals are present during precipitation in the form of coordination complexes, particularly tetra- and hexa-coordination complexes, both the metal ion and the coordination ligands can be occluded within the grains. Coordination ligands, such as halo, aquo, cyano, cyanate, fulminate, thiocyanate, selenocyanate, nitrosyl, thionitrosyl, oxo, carbonyl and ethylenediamine tetraacetic acid (EDTA) ligands have been disclosed and, in some instances, observed to modify emulsion

properties, as illustrated by Grzeskowiak U.S. Patent 4,847,191, McBugle et al U.S. Patents 4,933,272, 4,981,781, and 5,037,732; Marchetti et al U.S. Patent 4,937,180; Keever et al U.S. Patent 4,945,035; Hayashi U.S. Patent 5,112,732; Murakami et al EPO 0 509 674; Ohya et al EPO 0 513 738; Janusonis WO 91/10166; Beavers WO 92/16876; Fietsch et al German DD 298,320, and Olm et al U.S. 5,360,712.

Oligomeric coordination complexes can also be employed to modify grain properties, as illustrated by Evans et al U.S. Patent 5,024,931.

Dopants can be added in conjunction with addenda, antifoggants, dye, and stabilizers either during precipitation of the grains or post precipitation, possibly with halide ion addition. These methods may result in dopant deposits near or in a slightly subsurface fashion, possibly with modified emulsion effects, as illustrated by Ihama et al U.S. Patent 4,693,965; Shiba et al U.S. Patent 3,790,390; Habu et al U.S. Patent 4,147,542; Hasebe et al EPO 0 273 430; Ohshima et al EPO 0 312 999; and Ogawa U.S. Statutory Invention Registration H760.

Desensitizing or contrast increasing ions or complexes are typically dopants which function to trap photogenerated holes or electrons by introducing additional energy levels deep within the bandgap of the host material. Examples include, but are not limited to, simple salts and complexes of Groups 8-10 transition metals (e.g. rhodium, iridium, cobalt, ruthenium, and osmium), and transition metal complexes containing nitrosyl or thionitrosyl ligands as described by McBugle et al U.S. Patent 4,933,272.

Specific examples include K_3RhCl_6 , $(NH_4)_2Rh(CH_3)_2O$, K_2IrCl_6 , K_3IrCl_6 , K_2IrBr_6 , K_2RuCl_6 , $K_2Ru(NO)Br_5$, $K_2Ru(NS)Br_5$, K_2OsCl_6 , $Os_2O_5(NO)Cl_5$, and $K_2Os(NS)Cl_5$. Amine, oxalate, and organic ligand complexes of these or other metals as disclosed in Olm et al U.S. 5,360,712 are also specifically contemplated.

It is contemplated to incorporate in the face centered cubic crystal lattice a dopant capable of increasing photographic speed or other photographic features by forming shallow electron traps. When a photon is absorbed by a silver halide grain, an electron (hereinafter referred to as a photoelectron) is promoted from the valence band of the silver halide crystal lattice to its conduction band, creating a hole (hereinafter referred to as a photohole) in the valence band. To create a latent image site within the grain, a plurality of photoelectrons produced in a single image exposure must reduce several silver ions in the crystal lattice to form a small cluster of Ag^0 atoms. To the extent that photoelectrons are dissipated by competing mechanisms before the latent image can form, the photographic sensitivity of the silver halide grains is reduced. For example, if the photoelectron returns to the photohole, its energy is dissipated without contributing to latent image formation.

It is contemplated to dope the silver halide to create within it shallow electron traps that contribute to utilizing photoelectrons for latent image formation with greater efficiency. This is achieved by incorporating in the face centered cubic crystal lattice a dopant that exhibits a net valence more positive

than the net valence of the ion or ions it displaces in the crystal lattice. For example, in the simplest possible form the dopant can be a polyvalent (+2 to +5) metal ion that displaces silver ion (Ag^+) in the crystal lattice structure. The substitution of a divalent cation, for example, for the monovalent Ag^+ cation leaves the crystal lattice with a local net positive charge. This lowers the energy of the conduction band locally. The amount by which the local energy of the conduction band is lowered can be estimated by applying the effective mass approximation as described by J. F. Hamilton in the journal *Advances in Physics*, Vol. 37 (1988) p. 395 and *Excitonic Processes in Solids* by M. Ueta, H. Katsaki, K. Kobayashi, Y. Toyozawa and E. Hanamura (1986), published by Springer Verlag, Berlin, p. 359. If a silver chloride crystal lattice structure receives a net positive charge of +1 by doping, the energy of its conduction band is lowered in the vicinity of the dopant by about 0.048 electron volts (eV). For a net positive charge of +2 the shift is about 0.192 eV. For a silver bromide crystal lattice structure a net positive charge of +1 imparted by doping lowers the conduction band energy locally by about 0.026 eV. For a net positive charge of +2 the energy is lowered by about 0.104 eV.

When photoelectrons are generated by the absorption of light, they are attracted by the net positive charge at the dopant site and temporarily held (i.e., bound or trapped) at the dopant site with a binding energy that is equal to the local decrease in the conduction band energy. The dopant that causes the localized bending of the conduction band to a lower energy is referred to as a shallow electron trap because the binding energy holding the photoelectron at the dopant site (trap) is insufficient to hold the electron permanently at the dopant site. Nevertheless, shallow electron trapping sites are useful. For example, a large burst of photoelectrons generated by a high intensity exposure can be held briefly in shallow electron traps to protect them against immediate dissipation while still allowing their efficient migration over a period of time to latent image forming sites.

For a dopant to be useful in forming a shallow electron trap it must satisfy additional criteria beyond simply providing a net valence more positive than the net valence of the ion or ions it displaces in the crystal lattice. When a dopant is incorporated into the silver halide crystal lattice, it creates in the vicinity of the dopant new electron energy levels (orbitals) in addition to those energy levels or orbitals which comprised the silver halide valence and conduction bands. For a dopant to be useful as a shallow electron trap it must satisfy these additional criteria: (1) its highest energy electron occupied molecular orbital (HOMO), also commonly referred to as the frontier orbital) must be filled - e.g. if the orbital will hold two electrons (the maximum possible number), it must contain two electrons and not one and (2) its lowest energy unoccupied molecular orbital (LUMO) must be at a higher energy level than the lowest energy level conduction band of the silver halide crystal lattice. If conditions (1) and/or (2) are not satisfied, there will be a local, dopant-derived orbital in the crystal lattice (either an unfilled HOMO or a LUMO)

at a lower energy than the local, dopant-induced conduction band minimum energy, and photoelectrons will preferentially be held at this lower energy site and thus impede the efficient migration of photoelectrons to latent image forming sites.

Metal ions satisfying criteria (1) and (2) are the following: Group 2 metal ions with a valence of +2, Group 3 metal ions with a valence of +3 but excluding the rare earth elements 58-71, which do not satisfy criterion (1), Group 12 metal ions with a valence of +2 (but excluding Hg, which is a strong desensitizer, possibly because of spontaneous reversion to Hg²⁺), Group 13 metal ions with a valence of +3, Group 14 metal ions with a valence of +2 or +4 and Group 15 metal ions with a valence of +3 or +5. Of the metal ions satisfying criteria (1) and (2) those preferred on the basis of practical convenience for incorporation as dopants include the following period 4, 5 and 6 elements: lanthanum, zinc, cadmium, gallium, indium, thallium, germanium, tin, lead and bismuth. Specifically preferred metal ion dopants satisfying criteria (1) and (2) for use in forming shallow electron traps are zinc, cadmium, indium, lead and bismuth. Specific examples of shallow electron trap dopants of these types are provided by Demitt, Gilman et al, Atwell et al, Weyde et al and Narakima et al. EPO 0 590 674 and 0 563 946, each cited above and here incorporated by reference.

Metal ions in Groups 8, 9 and 10 (hereinafter collectively referred to as Group VIII metal ions) that have their frontier orbitals filled, thereby satisfying criterion (1), have also been investigated. These are Group 8 metal ions with a valence of +2, Group 9 metal ions with a valence of +3 and Group 10 metal ions with a valence of +4. It has been observed that these metal ions are incapable of forming efficient shallow electron traps when incorporated as bare metal ion dopants. This is attributed to the LUMO lying at an energy level below the lowest energy level conduction band of the silver halide crystal lattice.

However, coordination complexes of these Group VIII metal ions as well as Ga³⁺ and In³⁺, when employed as dopants, can form efficient shallow electron traps. The requirement of the frontier orbital of the metal ion being filled satisfies criterion (1).

For criterion (2) to be satisfied at least one of the ligands forming the coordination complex must be more strongly electron withdrawing than halide (i.e., more electron withdrawing than a fluoride ion, which is the most highly electron withdrawing halide ion).

One common way of assessing electron withdrawing characteristics is by reference to the spectrochemical series of ligands, derived from the absorption spectra of metal ion complexes in solution, referenced in *Inorganic Chemistry: Principles of Structure and Reactivity*, by James E. Huheey, 1972, Harper and Row, New York and *Absorption Spectra and Chemical Bonding in Complexes* by C. K. Jorgensen, 1962, Pergamon Press, London. From these references the following order of metal ions in the spectrochemical series is apparent: I⁻ < Br⁻ < S²⁻ < SCN⁻ < Cl⁻ < NO₃⁻ < F⁻ < OH⁻ < ox²⁻ < H₂O < NCS⁻ < CH₃CN⁻ < NH₃ < en < dipy < phen < NO₂⁻ < phosph < CN⁻ < CO. The abbreviations used are as

follows: ox = oxalate, dipy = dipyridine, phen = o-phenanthroline, and phosph = 4-methyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2]octane. The spectrochemical series places the ligands in sequence in their electron withdrawing properties, the first (I⁻) ligand in the series is the least electron withdrawing and the last (CO) ligand being the most electron withdrawing. The underlining indicates the site of ligand bonding to the polyvalent metal ion. The efficiency of a ligand in raising the LUMO value of the dopant complex increases as the ligand atom bound to the metal changes from Cl to S to O to N to C. Thus, the ligands CN⁻ and CO are especially preferred. Other preferred ligands are thiocyanate (NCS⁻), selenocyanate (NCSe⁻), cyanate (NCO⁻), tellurocyanate (NCte⁻) and azide (N₃⁻).

Just as the spectrochemical series can be applied to ligands of coordination complexes, it can also be applied to the metal ions. The following spectrochemical series of metal ions is reported in *Absorption Spectra and Chemical Bonding* by C. K. Jorgensen, 1962, Pergamon Press, London: Mn²⁺ < Ni²⁺ < Co²⁺ < Fe²⁺ < Cr³⁺ ≡ V³⁺ < Co³⁺ < Mn⁴⁺ < Mo³⁺ < Rh³⁺ ≡ Ru³⁺ < Pd⁴⁺ < Ir³⁺ < Pt⁴⁺. The metal ions in boldface type satisfy frontier orbital requirement (1) above. Although this listing does not contain all the metal ions which are specifically contemplated for use in coordination complexes as dopants, the position of the remaining metals in the spectrochemical series can be identified by noting that an ion's position in the series shifts from Mn²⁺, the least electronegative metal, toward Pt⁴⁺, the most electronegative metal, as the ion's place in the Periodic Table of Elements increases from period 4 to period 5 to period 6. The series position also shifts in the same direction when the positive charge increases. Thus, Os³⁺, a period 6 ion, is more electronegative than Pd⁴⁺, the most electronegative period 5 ion, but less electronegative than Pt⁴⁺, the most electronegative period 6 ion.

From the discussion above Rh³⁺, Ru³⁺, Pd⁴⁺, Ir³⁺, Os³⁺ and Pt⁴⁺ are clearly the most electronegative metal ions satisfying frontier orbital requirement (1) above and are therefore specifically preferred.

To satisfy the LUMO requirements of criterion (2) above the filled frontier orbital polyvalent metal ions of Group VIII are incorporated in a coordination complex containing ligands, at least one, most preferably at least 3, and optimally at least 4 of which are more electronegative than halide, with any remaining ligand or ligands being a halide ligand. When the metal ion is itself highly electronegative, such as Os³⁺, only a single strongly electronegative ligand, such as carbonyl, for example, is required to satisfy LUMO requirements. If the metal ion is itself of relatively low electronegativity, such as Fe²⁺, choosing all of the ligands to be highly electronegative may be required to satisfy LUMO requirements. For example, Fe(II)(CN)₆ is a specifically preferred shallow electron trapping dopant. In fact, coordination complexes containing 6 cyano ligands in general represent a convenient class of shallow electron trapping dopants.

Since Ga³⁺ and In³⁺ are capable of satisfying HOMO and LUMO

requirements as bare metal ions, when they are incorporated in coordination complexes they can contain ligands that range in electronegativity from halide ions to any of the more electronegative ligands useful with Group VIII metal ion coordination complexes.

For Group VIII metal ions and ligands of intermediate levels of electronegativity it can be readily determined whether a particular metal coordination complex contains the proper combination of metal and ligand electronegativity to satisfy LUMO requirements and hence act as a shallow electron trap. This can be done by employing electron paramagnetic resonance (EPR) spectroscopy. This analytical technique is widely used as an analytical method and is described in *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*, 2nd Ed., by Charles P. Poole, Jr. (1983) published by John Wiley & Sons, Inc., New York.

Photoelectrons in shallow electron traps give rise to an EPR signal very similar to that observed for photoelectrons in the conduction band energy levels of the silver halide crystal lattice. EPR signals from either shallow trapped electrons or conduction band electrons are referred to as electron EPR signals. Electron EPR signals are commonly characterized by a parameter called the g factor. The method for calculating the g factor of an EPR signal is given by C. P. Poole, cited above. The g factor of the electron EPR signal in the silver halide crystal lattice depends on the type of halide ion(s) in the vicinity of the electron. Thus, as reported by R.S. Eachus, M.T. Olm, R. Jones and M.C.R. Symons in the *Journal Physica Status Solidi (b)*, Vol. 152 (1989), pp. 583-592, in a AgCl crystal the g factor of the electron EPR signal is 1.88 ± 0.001 and in AgBr it is 1.49 ± 0.02 .

A coordination complex dopant can be identified as useful in forming shallow electron traps if, in the test emulsion set out below, it enhances the magnitude of the electron EPR signal by at least 20 percent compared to the corresponding undoped control emulsion. The undoped control emulsion is a $0.45 \pm 0.05 \mu\text{m}$ edge length AgBr octahedral emulsion precipitated, but not subsequently sensitized, as described for Control 1A of Marchetti et al U.S. Patent 4,937,180. The test emulsion is identically prepared, except that the metal coordination complex in the concentration intended to be used in the emulsion is substituted for $\text{Os}(\text{CN})_6^{4-}$ in Example 1B of Marchetti et al.

After precipitation, the test and control emulsions are each prepared for electron EPR signal measurement by first centrifuging the liquid emulsion, removing the supernatant, replacing the supernatant with an equivalent amount of warm distilled water and resuspending the emulsion. This procedure is repeated three times, and, after the final centrifuge step, the resulting powder is air dried. These procedures are performed under safe light conditions.

The EPR test is run by cooling three different samples of each emulsion to 20, 40 and 60°K, respectively, exposing each sample to the filtered output of a 200 W Hg lamp at a wavelength of 365 nm, and measuring the EPR electron signal during exposure.

If, at any of the selected observation temperatures, the intensity of the electron EPR signal is significantly enhanced (i.e., measurably increased above signal noise) in the doped test emulsion sample relative to the undoped control emulsion, the dopant is a shallow electron trap.

As a specific example of a test conducted as described above, when a commonly used shallow electron trapping dopant, $\text{Fe}(\text{CN})_6^{4-}$, was added during precipitation at a concentration of 50×10^{-6} dopant ions/silver mole as described above, the electron EPR signal intensity was enhanced by a factor of 8 over undoped control emulsion when examined at 20°K.

Hexacoordination complexes are preferred coordination complexes for use as shallow electron traps. They contain a metal ion and six ligands that displace a silver ion and six adjacent halide ions in the crystal lattice. One or two of the coordination sites can be occupied by neutral ligands, such as carbonyl, aquo or amine ligands, but the remainder of the ligands must be anionic to facilitate efficient incorporation of the coordination complex in the crystal lattice structure.

Illustrations of specifically contemplated hexacoordination complexes for are provided by McDugle et al U.S. Patent 5,037,732, Marchetti et al U.S. Patents 4,937,180, 5,264,336 and 5,268,264, Keever et al U.S. Patent 4,945,035, Murakami et al Japanese Patent Application Hei-2(1990)-249588, and Bell U.S. Patents 5,252,451 and 5,256,530 the disclosures of which are here incorporated by reference. Careful scientific investigations have revealed Group VIII hexahalo coordination complexes to create deep (desensitizing) electron traps, as illustrated R.S. Eachus, R.E. Graves and M.T. Olm *J. Chem. Phys.*, Vol. 69, pp. 4580-7 (1978) and *Physica Status Solidi A*, Vol. 57, 429-37 (1980).

In a specific, preferred form it is contemplated to employ as a dopant a hexacoordination complex satisfying the formula: $[\text{ML}_6]^n$ where M is filled frontier orbital polyvalent metal ion, preferably Fe^{2+} , Ru^{2+} , Os^{2+} , Co^{3+} , Rh^{3+} , Pd^{4+} , Pt^{4+} , L_6 represents six coordination complex ligands which can be independently selected, provided that least four of the ligands are anionic ligands and at least one (preferably at least 3 and optimally at least 4) of the ligands is more electronegative than any halide ligand; and n is -2, -3 or -4.

The following are specific illustrations of dopants capable of providing shallow electron traps:

$[\text{Fe}(\text{CN})_6]^{-4}$	SET-1	$[\text{Ru}(\text{CN})_6]^{-4}$	SET-2
$[\text{Os}(\text{CN})_6]^{-4}$	SET-3	$[\text{Rh}(\text{CN})_6]^{-3}$	SET-4
$[\text{Ir}(\text{CN})_6]^{-3}$	SET-5	$[\text{Fe}(\text{pyrazine})(\text{CN})_5]^{-4}$	SET-6
$[\text{RuCl}(\text{CN})_5]^{-4}$	SET-7	$[\text{OsBr}(\text{CN})_5]^{-4}$	SET-8
$[\text{RhF}(\text{CN})_5]^{-3}$	SET-9	$[\text{IrBr}(\text{CN})_5]^{-3}$	SET-10

[Fe(CN) ₅] ⁻³	SER-11	[Ru ₂ (CN) ₄] ⁻⁴	SER-12
[OsCl ₂ (CN) ₄] ⁻⁴	SER-13	[Rh ₁₂ (CN) ₄] ⁻³	SER-14
[IrBr ₂ (CN) ₄] ⁻³	SER-15	[Ru(CN) ₅ (OCN)] ⁻⁴	SER-16
[Ru(CN) ₅ (N ₃)] ⁻⁴	SER-17	[Os(CN) ₅ (SCN)] ⁻⁴	SER-18
[Rh(CN) ₅ (SecN)] ⁻³	SER-19	[Ir(CN) ₅ (HOH)] ⁻²	SER-20
[Fe(CN) ₅ 3Cl ₃] ⁻³	SER-21	[Ru(CO) ₂ (CN) ₄] ⁻¹	SER-22
[Os(CN) ₅ Cl ₅] ⁻⁴	SER-23	[Co(CN) ₆] ⁻³	SER-24
[Ir(NCS) ₆] ⁻³	SER-25	[In(NCS) ₆] ⁻³	SER-26
[Ga(NCS) ₆] ⁻³	SER-27		

It is additionally contemplated to employ oligomeric coordination complexes to increase speed, as taught by Evans et al U.S. Patent 5,024,931, the disclosure of which is here incorporated by reference.

The dopants are effective in conventional concentrations, where concentrations are based on the total silver, including both the silver in the grains and the silver in epitaxial protrusions. Generally shallow electron trap forming dopants are contemplated to be incorporated in concentrations of at least 1×10^{-6} mole per silver mole up to their solubility limit, typically up to about 5×10^{-4} mole per silver mole. Preferred concentrations are in the range of from about 10^{-5} to 10^{-4} mole per silver mole. It is, of course, possible to distribute the dopant so that a portion of it is incorporated in grains and the remainder is incorporated in the silver halide epitaxial protrusions.

C. Emulsion Addenda

Emulsion addenda that adsorb to grain surfaces, such as antifogants, stabilizers and dyes can also be added to the emulsions during precipitation. Precipitation in the presence of spectral sensitizing dyes is illustrated by Locker U.S. Patent 4,183,756, Locker et al U.S. Patent 4,225,666, Ihama et al U.S. Patents 4,683,193 and 4,828,972, Takagi et al U.S. Patent 4,912,017, Ishiguro et al U.S. Patent 4,983,508, Nakayama et al U.S. Patent 4,996,140, Steiger U.S. Patent 5,077,190, Brugger et al U.S. Patent 5,141,845, Metoki et al U.S. Patent 5,153,116, Asami et al EPO 0 287 100 and Tadaki et al EPO 0 301 508. Non-dye addenda are illustrated by Klotzer et al U.S. Patent 4,705,747, Ogi et al U.S. Patent 4,868,102, Ohya et al U.S. Patent 5,015,563, Bahmüller et al U.S. Patent 5,045,444, Maeka et al U.S. Patent 5,070,008, and Vandenberg et al EPO 0 392 092.

D. Emulsion Chemical Sensitization

Chemical sensitization of the materials in this photographic element is accomplished by any of a variety of known chemical sensitizers. The emulsions described herein may or may not have

other addenda such as sensitizing dyes, supersensitizers, emulsion ripeners, gelatin or halide conversion restainers present before, during or after the addition of chemical sensitization.

The use of sulfur, sulfur plus gold or gold only sensitizations are very effective sensitizers. Typical gold sensitizers are chloraurates, aurous dithiosulfate, aqueous colloidal gold sulfide or aurous bis(1,4,5-trimethyl-1,2,4-triazolium-3-thiolate) tetrafluoroborate (for example, see U.S. 5,049,485). Sulfur sensitizers may include thiosulfate, thiocyanate, *N,N'*-carbothioyl-bis(*N*-methylglycine) or 1,3-dicarboxymethyl-1,3-dimethyl-2-thiourea sodium salt.

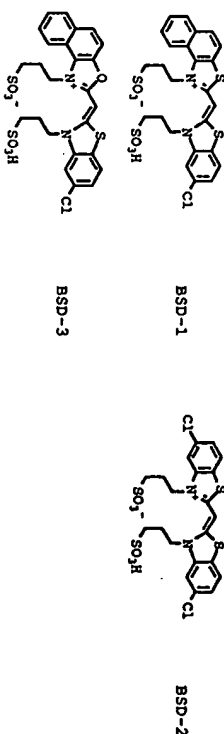
The addition of one or more antifogants as stain reducing agents is also common in silver halide systems. Tetrazindenes, such as 4-hydroxy-6-methyl(1,3,3a,7)-tetrazindene, are commonly used as stabilizers. Also useful are mercaptotetrazoles such as 1-phenyl-5-mercaptotetrazole or acetamido-1-phenyl-5-mercaptotetrazole. Arylthiosulfonates, such as tolylthiosulfonate (optionally used with arylsulfonates such as tolylsulfonate) or esters thereof are especially useful (e.g. see U.S. 4,960,689).

E. Spectral Sensitization

The emulsions can be spectrally sensitized with any of the dyes known to the photographic art, such as the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines, oxonols, hemioxonols, styryls, merostyryls and streptocyanines. In particular, it would be advantageous to select from among the low staining sensitizing dyes disclosed in USN 07/978,589 filed 11/19/92, and USN 07/978,568 filed 11/19/92, both granted, and European Patent Application Nos. 93/203,191.7 and 93/203,193.5. Use of low staining sensitizing dyes in a photographic element processed in a developer solution with little or no optical brightening agent (for instance, stilbene compounds such as Blankophor REUM) is specifically contemplated. Further, these low staining dyes can be used in combination with other dyes known to the art (Research Disclosure, September 1994, Item 36544, Section V).

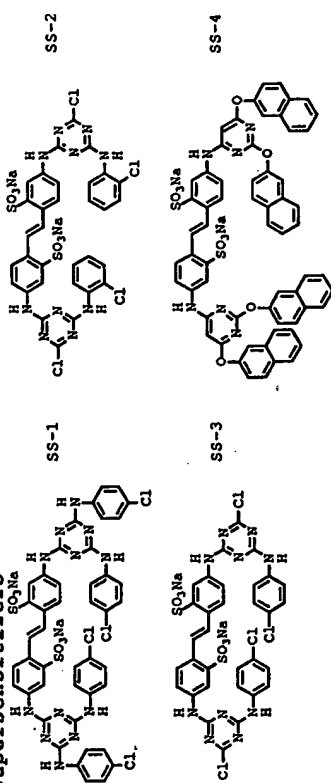
Useful sensitizing dyes include, but are not limited to, the following.

F. Structures of Typical Sensitizing Dyes



Photographic Science and Engineering, Vol. 18, 1974, pp. 418-430; and *Research Disclosure*, September 1994, Item 36544, Section V and references cited therein. Particularly useful are stilbene compounds as described in U.S. 4,945,038 and macrocyclic compounds as described in, for instance, U.S. 5,246,828. Useful supersensitizers include, but are not limited to the following.

Supersensitizers



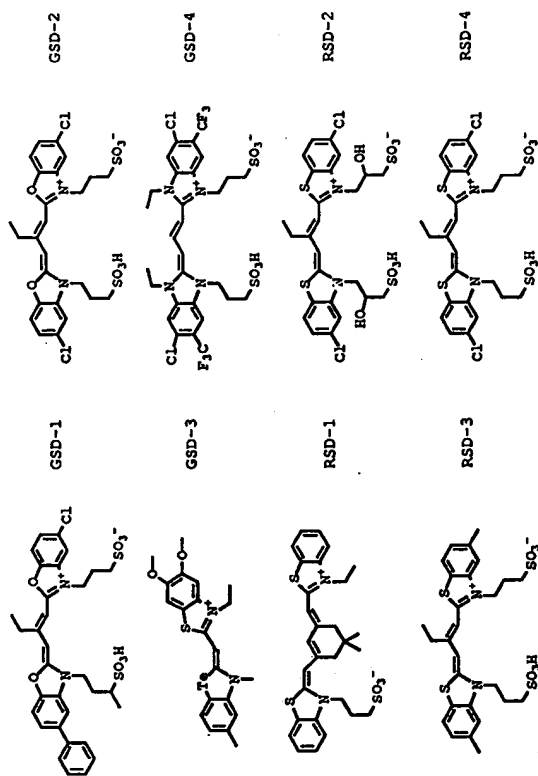
The photographic element may be coated on any suitable base material. Typically, this includes paper, polyesters (such as poly(ethylene terephthalate) and poly(ethylene naphthalate) and the materials described in U.S. 4,770,931; 4,942,005; and 5,156,905], and cellulose esters (such as cellulose triacetate), just to name several.

The photographic element may use any conventional peptizer material. A typical material utilized as a peptizer and carrier is gelatin. Such gelatin may be any of the conventional utilized gelatins for color paper or film. Preferred are the ossein gelatins. The element further may contain materials such as typically utilized in photographic elements including biostats, such as described in U.S. 4,490,462, fungicides, stabilizers, inter layers, overcoat protective layers.

If desired, the photographic element can be used in conjunction with an applied magnetic recording layer as described in *Research Disclosure*, November 1992, Item 34390.

XVI. Color Paper Embodiments

It is also contemplated that the concepts of the discussion may be employed to obtain reflection color prints as described in *Research Disclosure*, November 1979, Item 18716, incorporated herein by reference. The photographic element may contain epoxy solvents (EP 164,961); ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and stain reducing compounds such as described in U.S. Patent Nos. 5,068,171, 5,096,805, and 5,126,234. The particular base material utilized may be any material conventionally used in



Emulsions can be spectrally sensitized with mixtures of two or more sensitizing dyes which form mixed dye aggregates on the surface of the emulsion grain. The use of mixed dye aggregates enables adjustment of the spectral sensitivity of the emulsion to any wavelength between the extremes of the wavelengths of peak sensitivities (λ -max) of the two or more dyes. This practice is especially valuable if the two or more sensitizing dyes absorb in similar portions of the spectrum (i.e., blue, or green or red and not green plus red or blue plus red or green plus blue). Since the function of the spectral sensitizing dye is to modulate the information recorded in the negative which is recorded as an image dye, positioning the peak spectral sensitivity at or near the λ -max of the image dye in the color negative produces the optimum preferred response. In addition, the combination of similarly spectrally sensitized emulsions can be in one or more layers.

An important quality characteristic of a reproductive film system is color reproduction, which represents how accurately the hues of the original scene are reproduced. Many current color papers use a blue sensitizing dye that gives a maximum sensitivity at about 480 nm. Use of a sensitizing dye that affords a sensitivity maximum that is closer to that of the yellow image dye in film, for instance with a sensitivity maximum of around 450-470 nm, can result in a color paper with improved color reproduction.

It may be desirable to use combinations of dyes or dyes and addenda that provide supersensitization. For example, see Gilman,

silver halide color papers. Such materials are disclosed in *Research Disclosure*, September 1994, Item 36544, Section XV. It may be desired to coat the photographic element on pH adjusted support as described in U.S. 4,917,994. If desired, false sensitization, as described in Hahn in U.S. 4,902,609, can be used to provide added detail in color paper emulsions.

Any suitable base material may be utilized for the color paper. Typically, the base material is composed of bleached wood pulp fibers prepared by either the Kraft or Sulfite process, or both, but a base may be made (in whole or part) of wood fibers from mechanical pulping or semichemical pulping processes; from recycled fibers derived from either preconsumer or postconsumer waste paper; from non-wood plant fibers; or from synthetic polyolefin fibers, as known in the art. Alternatively, the base may be polymeric, such as one made of polyester. The wood fiber bases typically consist of any species of hardwood or softwood, or mixtures of these. Sheets formed from wood pulp may be created in either an acid or alkaline environment and contain numerous chemical additives. Such additives may include: polyamide epichlorohydrin resin or another suitable additive to increase wet strength; starch, polyacrylamide, polyacrylamide polyacrylic acid copolymer or similar additives to increase dry strength; long chain fatty acids (such as stearic), rosin, alkyl ketene dimer, alkanyl succinic anhydride or other suitable additives to provide sizing (resistance to liquid penetration); compounds, like those derived from diamnostilbenes, that absorb incident UV radiation and re-emit in the blue region of the spectrum to improve colorimetric properties, especially perceived whiteness; fillers and pigments, such as, titanium dioxide, clay, calcium carbonate, aluminum trihydrate, amorphous silicates, silicas or talc, which impart opacity and whiteness to the base, can control the optical properties and can improve archival keeping; acids and alkalis, like aluminum chloride, aluminum sulfate, polyaluminum chlorides and sulfates, aluminum hydroxychlorides, hydrochloric acid, sulfuric acid, sodium bicarbonate, sodium phosphates, sodium borates, sodium citrate, or sodium hydroxide can be used to control the pH (acidity and/or alkalinity) of the paper making process or the final sheet, to improve archival properties, and especially to improve emulsion keeping as described in U.S. Patent 4,994,147; polyvinyl alcohol (PVA, for example, see EP 553,339), starches (such as hydroxyethyl, hydroxypropyl, oxidized), styrene maleic anhydride and other strength enhancing, film forming chemicals applied at a size press unit operation to improve strength, surface, pore structure-related and image stability properties; antioxidants, such as *m*-cresol derivatives used for resin and emulsion stability; salts, like sodium chloride or sodium sulfate used to increase the conductivity of the paper sheet for static control in subsequent coating and winding operations; retention and drainage aids, like high molecular weight polyacrylamides or starches, used alone or in combination with microparticles, such as colloidal silica or bentonite clay; and defamers and biocides, employed as needed for process stability. The paper sheet is typically formed on a Fourdrinier

paper machine, but, as known in the art, could be made on a twin wire former or a cylinder former. The sheet is most often a single continuous ply, but multilayered sheets can also serve as a base sheet for this application. The paper base may be coated with a layer of pigment and binder to impart improved surface and optical properties prior to the polyolefin coating.

Due to a desire for rapid development, preferred emulsions for color paper are high in silver chloride. Typically, silver halide emulsions with greater than 90 mole % chloride are preferred, and even more preferred are emulsions of greater than 95 mole % chloride. In some instances, silver chloride emulsions containing small amounts of bromide, or iodide, or bromide and iodide are preferred, generally less than 5.0 mole % of bromide less than 2.0 mole % of iodide. Bromide or iodide addition when forming the emulsion may come from a soluble halide source such as potassium iodide or sodium bromide or an organic bromide or iodide or an inorganic insoluble halide such as silver bromide or silver iodide. Soluble bromide is also typically added to the emulsion melt as a keeping addendum.

Color paper elements typically contain less than 0.80 g/m² of total silver. Due to the need to decrease the environmental impact of color paper processing, it is desired to decrease the amount of total silver used in the element as much as possible. Therefore, total silver levels of less than 0.65 g/m² are preferable, and levels of 0.55 g/m² are even more preferable. It is possible to reduce further the total silver used in the color paper photographic element to less than 0.10 g/m² by use of a so-called development amplification process whereby the incorporated silver is used only to form the latent image, while another oxidant, such as hydrogen peroxide, serves as the primary oxidant to react with the color developer. Such processes are well-known to the art, and are described in, for example, U.S. 4,791,048; 4,880,725; and 4,954,425; EP 487,616; International published patent applications Nos. WO 90/013,059; 90/013,061; 91/016,666; 91/017,479; 92/001,972; 92/005,471; 92/007,299; 93/001,524; 93/011,460; and German published patent application OLS 4,211,460.

Typical color paper, color negative film, and color reversal film elements are described below.

XVII. Color Paper Example 1

Silver chloride emulsions were chemically and spectrally sensitized as is described below.

Blue Sensitive Emulsion (Blue EM-1, prepared similarly to that described in U.S. 5,252,451, column 8, lines 55-68): A high chloride silver halide emulsion was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. Cs₂O(NO₃)Cl₅ dopant was added during the silver halide grain formation for most of the precipitation, followed by a shearing without dopant. The resultant emulsion contained cubic shaped grains of 0.76 μ m in edge length size. This

emulsion was optimally sensitized by the addition of a colloidal suspension of aurous sulfide and heat ramped up to 60 °C during which time blue sensitizing dye BSD-1, 1-(3-acetamidophenyl)-5-mercaptotetrazole and potassium bromide were added. In addition, iridium dopant was added during the sensitization process.

Green Sensitive Emulsion (Green EM-1): A high chloride silver halide emulsion was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. $\text{Cs}_2\text{O}(\text{NO})\text{Cl}_5$ dopant was added during the silver halide grain formation for most of the precipitation, followed by a shell without dopant. Iridium dopant was added during the late stage of grain formation. The resultant emulsion contained cubic shaped grains of 0.30 μm in edgelenlength size. This emulsion was optimally sensitized by addition of green sensitizing dye GSD-1, a colloidal suspension of aurous sulfide, heat digestion followed by the addition of 1-(3-acetamidophenyl)-5-mercaptotetrazole and potassium bromide.

Red Sensitive Emulsion (Red EM-1): A high chloride silver halide emulsion was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. The resultant emulsion contained cubic shaped grains of 0.40 μm in edgelenlength size. This emulsion was optimally sensitized by the addition of a colloidal suspension of aurous sulfide followed by a heat ramp, and further additions of 1-(3-acetamidophenyl)-5-mercaptotetrazole, potassium bromide and red sensitizing dye RSD-1. In addition, iridium dopant was added during the sensitization process.

Red Sensitive Emulsion (Red EM-2): A high chloride silver halide emulsion was precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. The resultant emulsion contained cubic shaped grains of 0.40 μm in edgelenlength size. This emulsion was optimally sensitized by the addition of a colloidal suspension of aurous sulfide followed by a heat ramp, and further additions of 1-(3-acetamidophenyl)-5-mercaptotetrazole, potassium bromide, red sensitizing dye RSD-1, and supersensitizer SS-1. In addition, iridium dopant was added during the sensitization process.

Coupler dispersions were emulsified by methods well known to the art, and the following layers were coated on a polyethylene resin coated paper support, that was sized as described in U.S. Patent 4,994,147 and pH adjusted as described in U.S. Patent 4,917,994. The polyethylene layer coated on the emulsion side of the support contained a mixture of 0.1 % (4,4'-bis(5-methyl-2-benzoxazolyl) stilbene and 4,4'-bis(2-benzoxazolyl) stilbene, 12.5 % TiO_2 , and 3 % ZnO white pigment. The layers were hardened with bis(vinylsulfonfyl methyl) ether at 1.95 % of the total gelatin weight.

Layer 1: Blue Sensitive Layer

Gelatin	1.530 g/m ²
Blue Sensitive Silver (Blue EM-1)	0.280 g Ag/m ²
X-1	1.080 g/m ²
Dibutyl phthalate	0.260 g/m ²
2-(2-butoxyethoxy)ethyl acetate	0.260 g/m ²
2,5-Dihydroxy-5-methyl-3-(1-piperidinyl)-2-cyclopenten-1-one	0.002 g/m ²
SR-16	0.009 g/m ²

Layer 2: Interlayer

Gelatin	0.753 g/m ²
Diocetyl hydroquinone	0.094 g/m ²
Dibutyl phthalate	0.282 g/m ²
Sodium 4,5 Dihydroxy-m-benzenedisulfonate	0.065 g/m ²
SR-1	0.002 g/m ²

Layer 3: Green Sensitive Layer

Gelatin	1.270 g/m ²
Green Sensitive Silver (Green EM-1)	0.263 g Ag/m ²
M-1	0.389 g/m ²
Dibutyl phthalate	0.195 g/m ²
2-(2-butoxyethoxy)ethyl acetate	0.058 g/m ²
SR-2	0.166 g/m ²
Diocetyl hydroquinone	0.039 g/m ²
Phenylmercaptotetrazole	0.001 g/m ²

Layer 4: UV Interlayer

Gelatin	0.484 g/m ²
UV-1	0.028 g/m ²
UV-2	0.159 g/m ²
Diocetyl hydroquinone	0.038 g/m ²
1,4-Cyclohexylenedimethylene bis(2-ethylhexanoate)	0.062 g/m ²

Layer 5: Red Sensitive Layer

Gelatin	1.389 g/m ²
Red Sensitive Silver (Red EM-1)	0.187 g Ag/m ²
C-3	0.424 g/m ²
Dibutyl phthalate	0.414 g/m ²
UV-2	0.272 g/m ²
2-(2-butoxyethoxy)ethyl acetate	0.035 g/m ²
Diocetyl hydroquinone	0.004 g/m ²
Potassium tolylthiosulfonate	0.003 g/m ²
Potassium tolylsulfinate	0.0003 g/m ²

Layer 6: UV Overcoat

Gelatin	0.484 g/m ²
UV-1	0.028 g/m ²
UV-2	0.159 g/m ²
Diocetyl hydroquinone	0.038 g/m ²
1,4-Cyclohexylenedimethylene bis(2-ethylhexanoate)	0.062 g/m ²

Layer 7: SOC

Gelatin	1.076 g/m ²
Polydimethylsiloxane	0.027 g/m ²
SF-1	0.009 g/m ²
SF-2	0.004 g/m ²
Tergitol 15-S-5™	0.003 g/m ²
DYE-1	0.018 g/m ²
DYE-2	0.009 g/m ²
DYE-3	0.007 g/m ²

The coating described above is then repeated except that Red EM-2 is used in place of Red EM-1.

The coating described above is then repeated except the magenta layer is replaced with alternative magenta layer I.

Alternate Magenta Layer I

Layer 3: Green Sensitive Layer	
Gelatin	1.230 g/m ²
Green Sensitive Silver (Green EM-1)	0.160 g Ag/m ²
M-2	0.260 g/m ²
Tris(2-ethylhexyl)phosphate	0.520 g/m ²
ST-5	0.360 g/m ²
Dioctyl hydroquinone	0.060 g/m ²

The coating described above is then repeated except the magenta layer is replaced with alternative magenta layer II.

Alternate Magenta Layer II

Layer 3: Green Sensitive Layer	
Gelatin	1.230 g/m ²
Green Sensitive Silver (Green EM-1)	0.150 g Ag/m ²
M-7	0.215 g/m ²
Dibutyl phthalate	0.097 g/m ²
Di(8-methylnonyl)phthalate	0.086 g/m ²
ST-8	0.161 g/m ²
ST-19	0.140 g/m ²

The coating described above is then repeated except the magenta layer is replaced with alternative magenta layer III.

Alternate Magenta Layer III

Layer 3: Green Sensitive Layer	
Gelatin	1.230 g/m ²
Green Sensitive Silver (Green EM-1)	0.108 g Ag/m ²
M-10	0.140 g/m ²
Tricetyl phosphate	1.119 g/m ²
ST-1	0.129 g/m ²
ST-9	0.054 g/m ²
ST-10	0.097 g/m ²
ST-14	0.011 g/m ²

The coating described above is then repeated except the yellow layer is replaced with an alternative yellow layer I.

Alternate Yellow Layer I

Layer 1: Blue Sensitive Layer	
Gelatin	1.042 g/m ²
Blue Sensitive Silver (Blue EX-1)	0.243 g Ag/m ²
X-3	0.538 g/m ²
ST-6	0.237 g/m ²
ST-16	0.009 g/m ²
Dibutyl phthalate	0.301 g/m ²
Glycerol	0.162 g/m ²

The coating described above is then repeated except the yellow layer is replaced with an alternative yellow layer II.

Alternate Yellow Layer II

Layer 1: Blue Sensitive Layer	
Gelatin	1.042 g/m ²
Blue Sensitive Silver (Blue EX-1)	0.265 g Ag/m ²
X-4	0.538 g/m ²
ST-20	0.538 g/m ²
Dibutyl phthalate	0.269 g/m ²

XVIII. Color Paper Example 2

In a color paper format, the following materials may be coated with appropriately sensitized silver chloride emulsions on a support bearing the following layers from top to bottom:

- (1) one or more overcoats;
- (2) a cyan layer containing "Coupler 1": Butanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(3,5-dichloro-2-hydroxy-4-methylphenyl)-, "Coupler 2": Acetamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(3,5-dichloro-2-hydroxy-4-methylphenyl)-, "Coupler 3": Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-; Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-; Phenol, 2-(2H-benzotriazol-2-yl)-4-(1,1-dimethylethyl)-6-(1-methylpropyl)-; and Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)- and a poly(t-butylacrylamide) dye stabilizer;
- (3) an interlayer;
- (4) a magenta layer containing "Coupler 3": Octanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(2-(7-chloro-6-methyl-1H-pyrazolo[1,5-b][1,2,4]triazol-2-yl)propyl)- together with 1,1'-Spirobi(1H-indene), 2,2',3,3'-tetrahydro-3,3',3'-tetramethyl-5,5',6,6'-tetraepoxy-;
- (5) an interlayer; and
- (6) a yellow layer containing "Coupler 4": 1-Imidazolidineacetamide, N-(5-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-chlorophenyl)-4-(2,2-dimethyl-1-oxopropyl)-4-ethoxy-2,5-dioxo-3-(phenylmethyl)-.

XIX. Color Negative Example 1

A multilayer photographic negative element was produced by coating the following layers on a cellulose triacetate film support (coverage are in grams per meter squared, emulsion sizes as determined by the disc centrifuge method and are reported in Diameter x Thickness in microns).

Layer 1 (Antihalation layer): black colloidal silver sol at 0.151; gelatin at 2.44; UV-7 at 0.075; UV-8 at 0.075; DYE-5 at 0.042; DYE-6 at 0.088; DYE-7 at 0.020; DYE-8 at 0.008 and ST-17 at 0.161.

Layer 2 (Slow cyan layer): a blend of two silver iodobromide emulsions sensitized with a 1/9 mixture of RSD-3/RSD-4: (i) a small tabular emulsion (1.1 x 0.09, 4.1 mol % I) at 0.699; (ii) a very small tabular grain emulsion (0.5 x 0.08, 1.3 mol % I) at 0.492; gelatin at 1.78; cyan dye-forming coupler C-2 at 0.538; bleach accelerator releasing coupler C-22 at 0.038; masking coupler MC-1 at 0.027.

Layer 3 (Mid cyan layer): a red sensitized (same as above) silver iodobromide emulsion (1.3 x 0.12, 4.1 mol % I) at 0.699; gelatin at 1.79; C-2 at 0.204; D-6 at 0.010; MC-1 at 0.022.

Layer 4 (Fast cyan layer): a red-sensitized (same as above) tabular silver iodobromide emulsion (2.9 x 0.13, 4.1 mol % I) at 1.076; C-2 at 0.072; D-6 at 0.019; D-5 at 0.048; MC-1 at 0.032; gelatin at 1.42.

Layer 5 (interlayer): gelatin at 1.29.

Layer 6 (Slow magenta layer): a blend of two silver iodobromide emulsions sensitized with a 6/1 mixture of GSD-1/GSD-4: (i) 1.0 x 0.09, 4.1 mol % iodide at 0.308 and (ii) 0.5 x 0.08, 1.3 mol % I at 0.584; magenta dye forming coupler M-5 at 0.269; masking coupler MC-2 at 0.064; stabilizer ST-5 at 0.054; gelatin at 1.72.

Layer 7 (Mid magenta layer): a green sensitized (as above) silver iodobromide emulsion: 1.3 x 0.12, 4.1 mol % iodide at 0.968; M-5 at 0.071; MC-2 at 0.064; D-7 at 0.024; stabilizer ST-5 at 0.014; gelatin at 1.37.

Layer 8 (Fast magenta layer): a green sensitized (as above) tabular silver iodobromide (2.3 x 0.13, 4.1 mol % I) emulsion at 0.968; gelatin at 1.275; Coupler M-5 at 0.060; MC-2 at 0.054; D-1 at 0.001; D-4 at 0.001 and stabilizer ST-5 at 0.012.

Layer 9 (Yellow filter layer): DYE-4 at 0.108 and gelatin at 1.29.

Layer 10 (Slow yellow layer): a blend of three tabular silver iodobromide emulsions sensitized with sensitizing dye BSD-2: (i) 0.5 x 0.08, 1.3 mol % I at 0.295 (ii) 1.0 x 0.25, 6 mol % I at 0.50 and (iii) 0.81 x 0.087, 4.5 mol % I at 0.215; gelatin at 2.51; yellow dye forming couplers Y-15 at 0.725 and Y-14 at 0.289; D-3 at 0.064; C-2 at 0.027 and C-22 at 0.003.

Layer 11 (Fast yellow layer): a blend of two blue sensitized (as above) silver iodobromide emulsions: (i) a large tabular emulsion, 3.3 x 0.14, 4.1 mol % I at 0.227 and (ii) a 3-D emulsion, 1.1 x 0.4, 9 mol % I at 0.656; Y-15 at 0.725; Y-14 at 0.289; D-3 at 0.029; C-2 at 0.048; C-22 at 0.007 and gelatin at 2.57.

Layer 12 (UV filter layer): gelatin at 0.699; silver bromide Lippman emulsion at 0.215; UV-7 at 0.011 and UV-8 at 0.011.

Layer 13 (Protective overcoat): gelatin at 0.882.

Hardener (bis(vinylsulfonyl)methane hardener at 1.75% of total gelatin weight), antifoggants (including 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene), surfactants, coating aids, emulsion addenda, sequestrants, lubricants, matte and tinting dyes were added to the appropriate layers as is common in the art.

XX. Color Negative Example 2

For example, in a color negative element, the following materials may be coated with appropriately sensitized silver iodobromide emulsions on a support bearing the following layers from top to bottom:

(1) one or more overcoat layers containing ultraviolet absorber(s);

(2) a two-coat yellow pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-chloro-3-((2-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl)-3-(4-methoxyphenyl)-1,3-dioxopropyl)amino)-, dodecyl ester and a slow yellow layer containing the same compound together with "Coupler 2": Propionic acid, 2-[[5-[[4-[2-[[2,4-bis(1,1-dimethylpropyl)phenoxy]-acetyl]amino]-5-[[2,3,4,4,4-heptafluoro-1-oxobutyl]amino]-4-hydroxyphenoxy]-2,3-dihydroxy-6-[[propylamino)carbonyl]phenyl]-thio]-1,3,4-thiadiazol-2-yl]thio]-, methyl ester and "Coupler 3": 1-((dodecyl)carbonyl) ethyl(3-chloro-4-((3-(2-chloro-4-((1-tridecanoyloxy)carbonyl)anilino)-3-oxo-2-((4)(5)(6)-(phenoxycarbonyl)-1H-benzotriazol-1-yl)propanoyl)amino))-benzoate;

(3) an interlayer containing fine metallic silver;

(4) a triple-coat magenta pack with a fast magenta layer containing "Coupler 4": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-, "Coupler 5": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4',5'-dihydro-5'-oxo-1'-(2,4,6-trichlorophenyl)-1,4'-bi-1H-pyrazol-3'-yl)-, "Coupler 6": Carbamic acid, (6-((3-(dodecyl)oxy)propyl)amino)carbonyl-5-hydroxy-1-naphthalenyl)-2-methylpropyl ester, "Coupler 7": Acetic acid, ((2-((3-((3-(dodecyl)oxy)propyl)amino)carbonyl)-4-hydroxy-8-((2-methylpropoxy)carbonyl)amino)-1-naphthalenyl)oxyethyl)thio)-, and "Coupler 8": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)-phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-4-((4-methoxyphenyl)-azo)-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; a mid-magenta layer and a slow magenta layer each containing "Coupler 9": a ternary copolymer containing by weight in the ratio 1:1:2 2-Propenoic acid butyl ester, styrene, and N-(1-(2,4,6-trichlorophenyl)-4,5-dihydro-5-oxo-1H-pyrazol-3-yl)-2-methyl-2-propanamide; and "Coupler 10": Tetradecanamide, N-(4-chloro-3-((4-((1-(2,2-dimethyl-1-oxopropyl)amino)phenyl)azo)-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)amino)phenyl)-, in addition to Couplers 3 and 8;

(5) an interlayer;

(6) a triple-coat cyan pack with a fast cyan layer containing Couplers 6 and 7; a mid-cyan containing Coupler 6 and "Coupler 11": 2,7-Naphthalenedisulfonic acid, 5-(acetylamino)-3-((4-(2-

((3-(((3-(2,4-bis(1,1-dimethylpropyl)-phenoxy) propyl) amino) - carbonyl)-4-hydroxy-1-naphthalenyl) oxy)ethoxy)phenyl)azo)-4-hydroxy-, disodium salt; and a slow cyan layer containing Couplers 2 and 6;

(7) an undercoat layer containing Coupler 8; and
(8) an antihalation layer.

XXI. Color Reversal Example 1

A multilayer reversal film was prepared as follows. On a cellulose triacetate support provided with a subbing layer was coated each layer having the composition set forth below to prepare a multilayer color photographic light-sensitive material. In the composition of the layers, the coating amounts are shown as g/m² except for sensitizing dyes, which are shown as the molar amount per mole of silver halide present in the same layer. Emulsion sizes as determined by the disc centrifuge method and are reported in diameter x thickness in microns.

First layer: Antihalation Layer	
Black Colloidal Silver	0.43 (as Ag)
Gelatin	2.44
Second layer: Intermediate Layer	
Gelatin	1.22
Third layer: Slow Red Sensitive Layer	
AgBr tabular emulsion (4 & I, 0.6 x 0.1)	0.62 (as Ag)
RSD-2/RSD-3	1.42 x 10 ⁻³
C-23	0.20
Dibutyl phthalate	0.10
ST-18	0.06
Gelatin	0.86
Fourth layer: Fast Red Sensitive Layer	
AgBr tabular emulsion (4 & I, 0.97 x 0.13)	0.65 (as Ag)
RSD-2/RSD-3	1.05 x 10 ⁻³
C-23	1.00
Dibutyl phthalate	0.50
Gelatin	1.83
Fifth layer: Intermediate Layer	
DYE-9	0.07
ST-18	0.12
Gelatin	1.22
Sixth layer: Slow Green Sensitive Layer	
AgBr emulsion (3.3 & I, 0.15 cubic + 4 & I, 0.7 x 0.1 tabular)	0.70 (as Ag)
GSD-2/GSD-3	2.00 x 10 ⁻³
M-13	0.07
M-14	0.15
Trityl phosphate	0.11
Gelatin	0.83
Seventh layer: Fast Green Sensitive Layer	
AgBr tabular emulsion (4 & I, 0.97 x 0.13)	0.50 (as Ag)
GSD-2/GSD-3	1.00 x 10 ⁻³
M-13	0.32
M-14	0.74

Trityl phosphate

Gelatin

Eighth layer: Interlayer Layer

Gelatin

Ninth layer: Yellow Filter Layer

Caray Lea Silver

DYE-4

ST-18

Gelatin

Tenth layer: Slow Blue Sensitive Layer

AgBr tabular emulsion (3 & I, 1.1 x 0.12)

BSD-3

Y-15

Dibutyl phthalate

Gelatin

Eleventh layer: Fast Blue Sensitive Layer

AgBr tabular emulsion (3 & I, 1.7 x 0.1)

BSD-3

Y-15

Dibutyl phthalate

Gelatin

Twelfth layer: First Protective Layer

UV-1

UV-2

UV-7

ST-18

Gelatin

Thirteenth layer: Second Protective Layer

Fine grain AgBr emulsion

Matte

Bis(vinylsulfon)methane)

Gelatin

XXII. Color Reversal Example 2

In a reversal format, the following materials may be coated with appropriately sensitized silver iodobromide emulsions on a support bearing the following layers from top to bottom:

(1) one or more overcoat layers;

(2) a nonsensitized silver halide containing layer;

(3) a triple-coat yellow layer pack with a fast yellow layer containing "Coupler 1": Benzoic acid, 4-(1-((12-chloro-5-((dodecylsulfonyl)amino)phenyl)amino)carbonyl)-3,3-dimethyl-2-oxobutoxy)-, 1-methylethyl ester; a mid yellow layer containing Coupler 1 and "Coupler 2": Benzoic acid, 4-chloro-3-((12-(4-ethoxy-2,5-dioxo-3-(phenylmethyl)-1-imidazolidinyl)-4,4-dimethyl-1,3-dioxopentyl)amino)-, dodecylester; and a slow yellow layer also containing Coupler 2;

(4) an interlayer;

(5) a layer of fine-grained silver;

(6) an interlayer;

(7) a triple-coated magenta pack with a fast and mid magenta layer containing "Coupler 3": 2-Propenoic acid, butyl ester, polymer with N-(1-(2,5-dichlorophenyl)-4,5-dihydro-5-oxo-1H-

pyrazol-3-yl]-2-methyl-2-propenamide; "Coupler 4": Benzamide, 3-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-N-(4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1H-pyrazol-3-yl)-; and "Coupler 5": Benzamide, 3-((2,4-bis(1,1-dimethylpropyl)phenoxy)-1H-pyrazol-3-yl)-; and containing the stabilizer 1,1'-Spirobi(1H-indene), 2,2',3,3'-tetrahydro-3,3',3'-tetramethyl-5,5',6,6'-tetrapropoxy-; and in the slow magenta layer Couplers 4 and 5 with the same stabilizer;

(8) one or more interlayers possibly including fine-grained nonsensitized silver halide;

(9) a triple-coated cyan pack with a fast cyan layer containing "Coupler 6": Tetradecanamide, 2-(2-cyanophenoxy)-N-(4-((2,2,3,3,4,4-heptafluoro-1-oxobutyl)amino)-3-hydroxyphenyl)-; a mid cyan containing "Coupler 7": Butanamide, N-(4-((2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-1-oxobutyl)amino)-2-hydroxyphenyl)-2,2,3,3,4,4-heptafluoro- and "Coupler 8": Hexanamide, 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-((2,2,3,3,4,4-heptafluoro-1-oxobutyl)amino)-3-hydroxyphenyl)-; and a slow cyan layer containing Couplers 6, 7, and 8;

(10) one or more interlayers possibly including fine-grained nonsensitized silver halide; and

(11) an antibatation layer.

XXIII. Exposure and Processing

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and can then be processed to form a visible dye image. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known C-41 color process as described in *The British Journal of Photography Annual* of 1988, pages 191-198. Motion picture films may be processed as described in Kodak Publication No. H-24, Manual For Processing Eastman Color Films. Where applicable, the element may be processed in accordance with color print processes, such as the RA-4 process of Eastman Kodak Company as described in the *British Journal of Photography Annual* of 1988, pages 198-199, the Kodak Ektaprint 2 Process as described in Kodak Publication No. 2-122, using Kodak Ektaprint Chemicals, and the Kodak ECP Process as described in Kodak Publication No. H-24, Manual For Processing Eastman Color Films. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. For elements that lack incorporated dye image formers, sequential reversal color development with developers containing dye image formers such as color couplers is illustrated by the Kodachrome K-14 process (see U.S. Patent Nos 2,252,718;

2,950,970; and 3,547,650). For elements that contain incorporated color couplers, the E-6 color reversal process is described in the *British Journal of Photography Annual* of 1977, pages 194-197. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

In these color photographic systems, the color-forming coupler is incorporated in the light-sensitive photographic emulsion layer so that during development, it is available in the emulsion layer to react with the color developing agent that is oxidized by silver image development. Diffusible couplers are used in color developer solutions. Non-diffusing couplers are incorporated in photographic emulsion layers. When the dye image formed is to be used in situ, couplers are selected which form non-diffusing dyes. For image-transfer color processes, couplers are used which will produce diffusible dyes capable of being mordanted or fixed in the receiving sheet. The color photographic systems described can also be used to produce black-and-white images from non-diffusing couplers as described by Edwards et al in International Publication No. WO 93/012465.

Photographic color light-sensitive materials often utilize silver halide emulsions where the halide, for example chloride, bromide and iodide, is present as a mixture or combination of at least two halides. The combinations significantly influence the performance characteristics of the silver halide emulsion. As explained in Atwell, U.S. Pat. No. 4,269,927, silver halide with a high chloride content, that is, light-sensitive materials in which the silver halide grains are at least 80 mole percent silver chloride, possesses a number of highly advantageous characteristics. For example, silver chloride possesses less native sensitivity in the visible region of the spectrum than silver bromide, thereby permitting yellow filter layers to be omitted from multicolor photographic light-sensitive materials. However, if desired, the use of yellow filter layers should not be excluded from consideration for a light sensitive material. Furthermore, high chloride silver halides are more soluble than high bromide silver halides, thereby permitting development to be achieved in shorter times. Furthermore, the release of chloride into the developing solution has less restraining action on development compared to bromide and this allows developing solutions to be utilized in a manner that reduces the amount of waste developing solution.

Processing a silver halide color photographic light-sensitive material is basically composed of two steps of 1) color development (for color reversal light-sensitive materials, black-and-white first development is necessary) and 2) desilvering. The desilvering stage comprises a bleaching step to change the developed silver back to an ionic-silver state and a fixing step to remove the ionic silver from the light-sensitive material. The bleaching and fixing steps can be combined into a monobath bleach-fix step that can be used alone or in combination with the bleaching and the fixing step. If necessary, additional processing steps may be added, such as a washing step, a stopping step, a stabilizing step and a pretreatment step to accelerate development. The processing chemicals used may be liquids,

pastes, or solids, such as powders, tablets or granules.

In color development, silver halide that has been exposed to light (or a reversal bath for color reversal) is reduced to silver, and at the same time, the oxidized aromatic primary amine color developing agent is consumed by the above mentioned reaction to form image dyes. In this process halide ions from the silver halide grains are dissolved into the developer, where they will accumulate. In addition the color developing agent is consumed by the aforementioned reaction of the oxidized color developing agent with the coupler. Furthermore, other components in the color developer will also be consumed and the concentration will gradually be lowered as additional development occurs. In a batch-processing method, the performance of the developer solution will eventually be degraded as a result of the halide ion build-up and the consumption of developer components. Therefore, in a development method that continuously processes a large amount of a silver halide photographic light-sensitive material, for example by automatic-developing processors, in order to avoid a change in the finished photographic characteristics caused by the change in the concentrations of the components, some means is required to keep the concentrations of the components of the color developer within certain ranges.

For instance, a developer solution in a processor tank can be maintained at a 'steady-state concentration' by the use of another solution that is called the replenisher solution. By metering the replenisher solution into the tank at a rate proportional to the amount of the photographic light-sensitive material being developed, components can be maintained at an equilibrium within a concentration range that will give good performance. For the components that are consumed, such as the developing agents and preservatives, the replenisher solution is prepared with the component at a concentration higher than the tank concentration. In some cases a material will leave the emulsion layers that will have an effect of restraining development, and will be present at a lower concentration in the replenisher or not present at all. In other cases a material may be contained in a replenisher in order to remove the influence of a materials that will wash out of the photographic light-sensitive material. In other cases, for example, the buffer, or the concentration of a chelating agent where there may be no consumption, the component in the replenisher is the same or similar concentration as in the processor tank. Typically the replenisher has a higher pH to account for the acid that is released during development and coupling reactions so that the tank pH can be maintained at an optimum value.

Similarly, replenishers are also designed for the secondary bleach, fixer and stabilizer solutions. In addition to additions for components that are consumed, components are added to compensate for the dilution of the tank which occurs when the previous solution is carried into the tank by the photographic light-sensitive material.

The following processing steps may be included in the preferable processing steps carried out in the method in which a processing solution is applied:

- 1) color developing → bleach-fixing → washing/stabilizing;
- 2) color developing → bleaching → fixing → washing/stabilizing;
- 3) color developing → bleaching → bleach-fixing → washing/stabilizing;
- 4) color developing → stopping → washing → bleaching → washing → fixing → bleaching-fixing → fixing → washing/stabilizing;
- 5) color developing → bleach-fixing → fixing → washing/stabilizing;
- 6) color developing → bleaching → bleach-fixing → fixing → washing/stabilizing.

Among the processing steps indicated above, the steps 1), 2), 3), and 4) are preferably applied. Additionally, each of the steps indicated can be used with multistage applications as described in Hahn, U.S. Pat. No. 4,719,173, with co-current, counter-current, and contraco arrangements for replenishment and operation of the multistage processor.

Any photographic processor known to the art can be used to process the photosensitive materials described herein. For instance, large volume processors, and so-called minilab and microlab processors may be used. Particularly advantageous would be the use of low volume Thin Tank processors as described in the following references: WO 92/10790; WO 92/17819; WO 93/04404; WO 92/17370; WO 91/19226; WO 91/12567; WO 92/07302; WO 93/00612; WO 92/07301; WO 92/09932; U.S. 5,294,956; EP 559,027; U.S. 5,179,404; EP 559,025; U.S. 5,270,762; EP 559,026; U.S. 5,313,243; U.S. 5,339,131.

A. Color Paper Process

The color developing solution used with this photographic element may contain aromatic primary amine color developing agents, which are well known and widely used in a variety of color photographic processes. Preferred examples are *p*-phenylenediamine derivatives. They are usually added to the formulation in a salt form, such as the hydrochloride, sulfate, sulfite, *p*-toluenesulfonate, as the salt form is more stable and has a higher aqueous solubility than the free amine. Among the salts listed the *p*-toluenesulfonate is rather useful from the viewpoint of making a color developing agent highly concentrated. Representative examples are given below, but they are not meant to limit what could be used with the present photographic element:

- 4-amino-3-methyl-*N*-ethyl-*N*-(β -hydroxyethyl)aniline sulfate,
- 4-amino-3-methyl-*N*-ethyl-*N*-(β -(methanesulfonamidoethyl)aniline sesquisulfate hydrate,
- 4-amino-*N,N*-diethylaniline hydrochloride,
- 4-amino-3-methyl-*N,N*-diethylaniline hydrochloride,
- 4-amino-3- β -(methanesulfonamido)ethyl-*N,N*-diethylaniline hydrochloride and
- 4-amino-*N*-ethyl-*N*-(2-methoxyethyl)-*m*-toluidine di-*p*-toluene

sulfonic acid.

Among the above-mentioned color developing agents, the first two may preferably be used. There may be some instances where the above mentioned color developing agents may be used in combination so that they meet the purposes of the application.

The color developing agent is generally employed in concentrations of from 0.0002 to 0.2 M of developing solution and more preferably from about 0.001 to 0.05 M of developing solution.

The developing solution should also contain chloride ions in the range 0.006 to 0.33 M, preferably 0.02 to 0.16 M and bromide ions in the range of zero to 0.001 M, preferably 2×10^{-5} to 5×10^{-4} M. The chloride ions and bromide ions may be added directly to the developer or they may be allowed to dissolve out from the photographic material in the developer and may be supplied from the emulsion or a source other than the emulsion.

If chloride is added directly to the color developer, the chloride-ion-supplying salt can be (although not limited to) sodium chloride, potassium chloride, ammonium chloride, lithium chloride, magnesium chloride, manganese chloride, and calcium chloride, with sodium chloride and potassium chloride preferred.

If bromide is added directly to the color developer, the bromide-ion-supplying salt can be (although not limited to) sodium bromide, potassium bromide, ammonium bromide, lithium bromide, calcium bromide, and manganese bromide, with sodium bromide and potassium bromide preferred.

The chloride-ions and bromide-ions may be supplied as a counter ion for another component of the developer, for example the counter ion for a stain reducing agent.

Preferably, the pH of the color developer is in the range of 9 to 12, more preferably 9.6 to 11.0 and it can contain other known components of a conventional developing solution.

To maintain the above-mentioned pH, it is preferable to use various buffer agents. Examples of buffer agents that can be mentioned include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate) and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate). Preferably the amount of buffer agent to be added is 0.1 M to 0.4 M.

Additional components of the developer include preservatives to protect the color developing agent from decomposition. The 'preservative' is characterized as a compound that generally can reduce the rate of decomposition of the color developing agent. When it is added to the processing solution for the color photographic material it prevents the oxidation of the color developing agent caused by oxygen in the air. It is preferable that the developer contain an organic preservative. Particular examples include hydroxylamine derivatives (but excluding hydroxylamine, as described later), hydrazines, hydrazides, hydroxamic acids, phenols, aminoketones, saccharides, monoamines,

diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds, and condensed ring-type amines.

For the preferable organic preservatives mentioned above, typical compounds are mentioned below. It is desirable that the amount of the compounds mentioned below be added to the developer solution at a concentration of 0.005 to 0.5 M, and preferably 0.025 to 0.1 M.

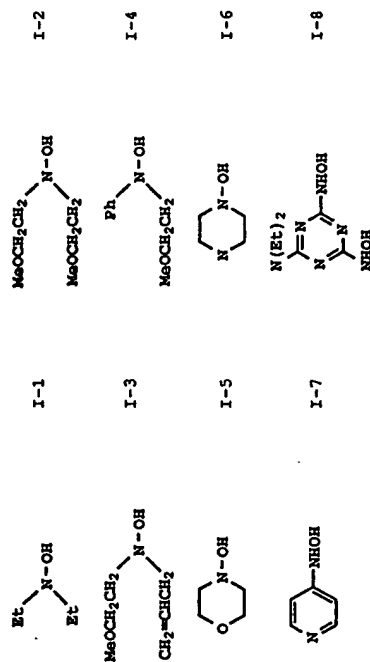
As hydroxylamine derivatives, the following are preferable:



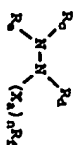
where R_a and R_b each represent a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heteroaromatic group, they do not represent hydrogen atoms at the same time, and they may bond together to form a heterocyclic ring with the nitrogen atom. The ring structure of the heterocyclic ring is a 5-6 member ring, it is made up of carbon atoms, oxygen atoms, nitrogen atoms, sulfur atoms, etc. and it may be saturated or unsaturated.

It is preferable that R_a and R_b each represent an alkyl group or an alkenyl group having 1 to 5 carbon atoms. As nitrogen containing heterocyclic rings formed by bonding R_a and R_b together examples are a piperidyl group, a pyrrolidyl group, an N-alkylpiperazyl group, a morpholyl group, an indolyl group, and a benzotriazolyl group.

Preferable substituents of R_a and R_b are a hydroxyl group, an alkoxy group, an alkylsulfonyl group, an arylsulfonyl group, an amido group, a carboxyl group, a sulfo group, a nitro group, and an amino group. Exemplified compounds are:



The hydrazines and hydrazides preferably include those represented by the formula II:



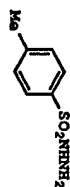
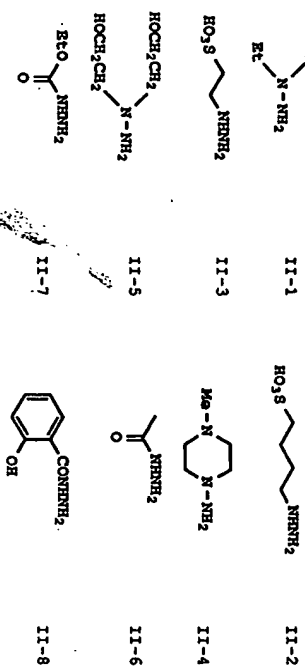
Formula (II)

where R_0 , R_1 , and R_2 , which may be the same or different,

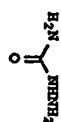
represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group; R_3 represents a hydroxyl group, a hydroxylamino group, a substituted or unsubstituted alkyl group, a substituted or unsubstituted amino group, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group comprising carbon, oxygen, nitrogen, sulfur atoms, etc.; R_4 represents a divalent group selected from $-CO-$, $-SO_2-$ and $>C=NH$ and n represents 0 or 1; provided that when n is 0, R_1 is selected from an alkyl group, an aryl group, and a heterocyclic group; R_3 and R_4 may combine to form a heterocyclic group.

In formula (II) R_0 , R_1 , R_2 each preferably represents a hydrogen atom or an alkyl group having from 1 to 10 carbon atoms. R_3 and R_4 each more preferably represent a hydrogen atom. R_3 preferably represents an alkyl group, an aryl group, an alkoxy group, a carbamoyl group, or an amino group, and more preferably an alkyl group or a substituted alkyl group. Preferred substituents on the alkyl group include a carboxyl group, a sulfo group, a nitro group, an amino group, a phosphono group, etc. R_4 preferably represents $-CO-$ or $-SO_2-$, and most preferably represents $-CO-$.

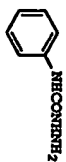
Specific examples of the hydrazines and hydrazides represented by formula (II) are shown below.



II-9



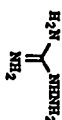
II-10



II-11



II-12



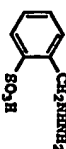
II-13



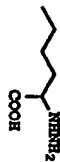
II-14



II-15



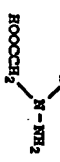
II-16



II-17



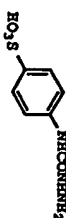
II-18



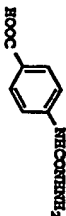
II-19



II-20



II-21



II-22

Other organic preservatives of potential use are mentioned by Yoshida, et. al., in U.S. Pat. No. 5,077,180 with lists of examples from each of the classes for the following organic preservative classes: hydroxamic acids, phenols, amideketones, saccharides, monamines, diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds, and condensed ring-type amines. Additionally, a sulfonic acid or salt thereof may be used to improve the stability of the color developing agent in concentrated solutions, with examples described by Nakamura, et. al., in U.S. Pat. No. 5,204,229.

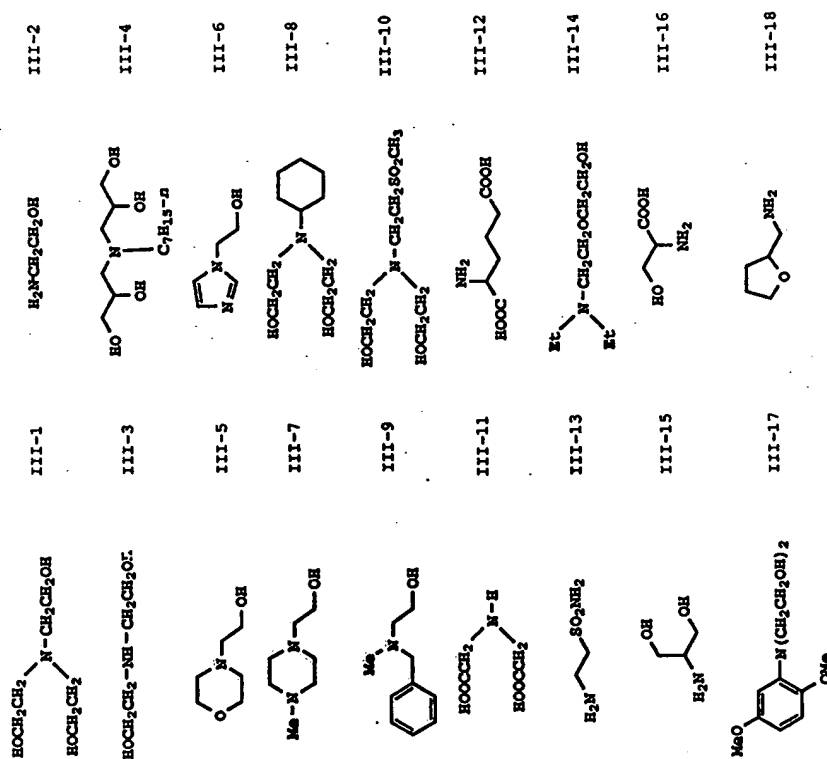
A further ingredient which can optionally be included in the color developing composition to improve the stability of the color developer and assure stable continuous processing represented by formula (III):



Formula (III)

where R_1 , R_2 , R_3 , and R_4 each represents a hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted heterocyclic group, or R_2 and R_3 , R_3 and R_4 , or R_1 and R_4 .

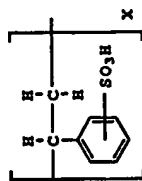
and R₁ may combine to form a nitrogen-containing heterocyclic ring. As described in Case et. al. U.S. Pat. No. 4,170,478 a preferred example of formula (III) are alkanolamines, wherein R₉ is an hydroxyalkyl group and each of R₈ and R₁ is a hydrogen atom, an alkyl group, a hydroxyalkyl group, an aryl group, or a -C_nH_{2n}N(Y)₂ group, wherein n is an integer of from 1 to 6 and each of Y and Z is a hydrogen atom, an alkyl group or an hydroxyalkyl group. Specific examples of the amine and hydroxylamine compounds represented by formula (III) are shown below.



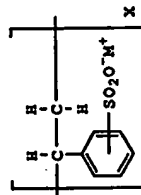
A small amount of sulfite can optionally be incorporated in the developing compositions to provide additional protection against oxidation. In view of the fact that sulfite competes in the developer with coupler for oxidized developing agent and can have a resultant effect to decrease the desired image dye formation, it is preferred that the amount of sulfite be very small, for example in the range from zero to 0.04 M. The use of a small amount of sulfite is especially desirable when the color developing composition is packaged in a concentrated form to preserve the concentrated solution from oxidation.

It is preferable that the developer is substantially free of hydroxylamine, often used as a developer preservative. This is because hydroxylamine has an undesired effect on the silver development and results in low yields of image dye formation. The expression 'substantially-free from hydroxylamine' means that the developer contains only 0.005 M or below of hydroxylamine per liter of developer solution.

To improve the clarity of the working developer solution and reduce the tendency for tarring to take place it is preferred to incorporate therein a water-soluble sulfonated polystyrene. The sulfonated polystyrene can be used in the free acid form or in the salt form. The free acid form of the sulfonated polystyrene is comprised of units having the formula:



where X is an integer representing the number of repeating units in the polymer chain and is typically in the range from about 10 to about 3,000 and more preferably in the range from about 100 to 1,000. The salt form of the sulfonated polystyrene is comprised of units having the formula:



where X is as defined above and M is a monovalent cation, such as, for example, an alkali metal ion.

The sulfonated polystyrenes utilized in the developing compositions can be substituted with substituents such as halogen atoms, hydroxy groups, and substituted or unsubstituted alkyl groups. For example, they can be sulfonated derivatives of chlorostyrene, alpha-methyl styrene, vinyl toluene, and the like. Neither the molecular weight nor the degree of sulfonation are critical, except that the molecular weight should not be so high nor the degree of sulfonation so low as to render the sulfonated polystyrene insoluble in aqueous alkaline photographic color developing solutions. Typically, the average degree of sulfonation, that is the number of sulfonic acid groups per repeating styrene unit, is in the range from about 0.5 to 4 and more preferably in the range from about 1 to 2.5. A variety of salts of the sulfonated polystyrene can be employed, including, in addition to alkali metal salts, the amine salts such as salts of monoethanolamine, diethanolamine, triethanolamine, morpholine, pyridine, picoline, quinoline, and the like.

The sulfonated polystyrene can be used in the working developer solution in any effective amount. Typically, it is employed in amount of from about 0.05 to about 30 grams per liter of developer solution, more usually in amount of from about 0.1 to about 15 grams per liter, and preferably in amounts of from 0.2 to about 5 grams per liter.

In addition various chelating agents may also be added to the developer to prevent calcium or magnesium from precipitating or to improve the stability of the color developer. Specific examples are shown below, but use with the present photographic element is not limited to them:

nitrotriacetic acid,
diethylenetriaminopentacetic acid,
ethylenediaminetetraacetic acid,
triethylenetetraaminohexaacetic acid,
N,N'-trimethylenephosphonic acid,
ethylenediamine-N,N',N''-tetramethylenephosphonic acid,
1,3-diamino-2-propanoltetraacetic acid,
trans-cyclohexanediaminetetraacetic acid,
nitrotridipropionic acid,
1,2-diaminopropanetetraacetic acid,
hydroxyethyliminodiacetic acid,
glycol ether diaminetetraacetic acid,
hydroxyethylenediaminetriacetic acid,
ethylenediamine-o-hydroxyphenylacetic acid,
2-phosphonobutane-1,2,4-tricarboxylic acid,
1-hydroxyethylidene-1,1-diphosphonic acid,
N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N''-diacetate,
N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N''-diacetic acid,
catechol-3,4,6-trisulfonic acid,
catechol-3,5-disulfonic acid,
5-sulfosalicylic acid,
4-sulfosalicylic acid,
β-alaninediacetic acid,
and glycinedipropionic acid.

A particularly useful chelating agent for photographic color developer compositions are the hydroxyalkylidene diphosphonic acid of the formula:



where R₁ is an alkyl or substituted alkyl group. When R₁ is an ethyl group a preferred chelating agent example, is 1-hydroxyethylidene-1,1-diphosphonic acid. The hydroxyalkylidene diphosphonic acid chelating agents can serve as both the chelating agent which functions to sequester iron and which functions to sequester both iron and calcium. As described in Brown, U.S. Pat. No. 3,839,045, they are preferably utilized in combination with small amounts of lithium salts, such as lithium sulfate or lithium chloride.

The chelating agents can be utilized in the form of a free acid or in the form of a water soluble salt form. If desired, the above mentioned chelating agents may be used as a combination of two or more. One preferred combination is demonstrated by Buongiorno, et. al., U.S. Pat. No. 4,975,357 as a combination of the class of polyhydroxy compounds, such as catechol-3,5-disulfonic acid, and of the class of an aminoarboxylic acid, such as ethylenetriamine pentacetic acid.

It is preferable that the color developer be substantially free of benzyl alcohol. Herein the term 'substantially free of benzyl alcohol' means that the amount of benzyl alcohol is no more than 2 ml per liter, but even more preferably benzyl alcohol should not be contained at all.

It is preferred that the color developer contain a triazinyl stilbene type stain reducing agent, which is often referred to as a fluorescent whitening agent. There are a wide variety of effective stain reducing agents, preferred examples include Blankophor REU, and Tinopal SFP. The triazinyl stilbene type of stain reducing agent may be used in an amount within the range of, preferably 0.2 grams to 10 grams per liter of developer solution and more preferably, 0.4 to 5 grams per liter.

In addition, compounds can be added to the color developing solution to increase the solubility of the developing agent. Examples of materials, if required, include methyl cellosolve, methanol, acetone, dimethyl formamide, cyclodextrin, dimethyl formamide, diethylene glycol, and ethylene glycol.

It is also mentioned that the color developer solution may contain an auxiliary developing agent together with the color developing agent. Examples of known auxiliary developing agents include for example, N-methyl-p-aminophenol sulfate, phenidone, N,N'-diethyl-p-aminophenol hydrochloride and an N,N,N',N'-tetramethyl-p-phenylenediamine hydrochloride. The auxiliary developing agent may be added in an amount within the range of,

typically, 0.01 to 1.0 grams per liter of color developer solution.

It may be preferable, if required to enhance the effects of the color developer, to include an anionic, cationic, amphoteric and nonionic surfactant. If necessary, various other components may be added to the color developer solution, including dye-forming couplers, competitive couplers, and fogging agents such as sodium borohydride.

If desired, the color developing agent may contain an appropriate development accelerator. Examples of development accelerators include thioether compound as described in U.S. Patent 3,813,247; quaternary ammonium salts; the amine compounds as described in U.S. Pat. Nos. 2,494,903, 3,128,182, 3,253,919, and 4,230,796; the polyalkylene oxides as described in U.S. Pat. No. 3,532,501.

An antifoggant may be added if required. Antifoggants that can be added include alkali metal halides, such as sodium or potassium chloride, sodium or potassium bromide, sodium or potassium iodide and organic antifoggants. Representative examples of organic antifoggants include nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolylbenzimidazole, 2-thiazolyl-methylbenzimidazole, indazoles, hydroxyazindoline, and adenine.

The above mentioned color developer solutions may be used at a processing temperature of preferably 25 °C to 45 °C and more preferably from 35 °C to 45 °C. Further, the color developer solution may be used with a processing time in the developer step of the process with a time of not longer than 240 seconds and preferably within a range from 3 seconds to 110 seconds, and more preferably not shorter than 5 seconds and not longer than 45 seconds.

As previously described, a color developer processing tank in a continuous processor is replenished with a replenisher solution to maintain the correct concentration of color developer solution components. The color developer replenisher solution may be replenished in an amount of, ordinarily not more than 500 mL per square meter of a light sensitive material. Since replenishment results in a quantity of waste solution, the rate of replenishment is preferably minimized so that waste volume and costs can be minimized. A preferred replenishment rate is within a range of 10 to 215 mL per square meter, and more preferably 25 to 160 mL per square meter.

Additionally the developer waste volume and material costs may be reduced by recovering the overflow from the developer tank as it is being replenished and treating the overflow solution in a manner so that the overflow solution can be used again as a replenisher solution. In one operating mode, chemicals are added to the overflow solution to make up for the loss of chemicals from that tank solution that resulted from the consumption of chemicals that occurred during the development reactions. The chemicals can be added as solid components or as aqueous solutions of the component chemicals. Addition of water and the aqueous solutions of the make-up chemicals also have the effect to reduce the

concentration of the materials that wash out of the light-sensitive material and are present in the developer overflow. This dilution of materials that wash out of the light-sensitive material prevents concentration of these materials from increasing to concentrations that can lead to undesired photographic effects, reduced solution stability, and precipitates. The method for the regeneration of a developer is described in Kodak Publication No. 2-130, 'Using EKTACOLOR RA Chemicals'. If the materials that wash out of the light-sensitive material are found to increase to an objectionable concentration, the overflow solution can be treated to remove the objectionable material. Ion-exchange resins, cationic, anionic and amphoteric are especially well suited to remove specific components found to be objectionable.

The recovery of developer solution overflow can be characterized as the percentage of the original replenisher solution that is recovered and reused, thus a 55% 'reuse ratio' indicates that of the original replenisher volume used, 55% of the original volume was recovered and reused. A packaged chemical mix of concentrated chemical solutions concentrates can be designed to be used with a designated amount of overflow to produce a replenisher solution for use in the continuous processor being used to process the light sensitive material. While it is useful to be able to recover any amount of developer overflow solution, it is preferable to be able to recover at least 50% (ie. a 50% reuse ratio) of the developer overflow. It is preferred to have a reuse ratio of 50% to 75% and it is more preferred to have a reuse ratio of 50% to 95%.

It is an objective for use with the current photographic element to produce a color photographic light sensitive material where substantially all of the silver that was originally used in producing the photographic images is removed from the light-sensitive material during the processing stage. In a preferred example, both the developed and undeveloped silver is removed in a single processing step using a bleach-fix solution.

The components of a bleach-fix solution are comprised of silver halide solvents, preservatives, bleaching agents, chelating agents, acids, and bases. Each of the components may be used as single components or as mixtures of two or more components.

As silver solvents, thiosulfates, thiocyanates, thioether compounds, thioureas, and thioglycolic acid can be used. A preferred component is thiosulfate, and ammonium thiosulfate, in particular is used most commonly owing to the high solubility. If desired, other counter ions may be used in place of ammonium ion. Alternative counter-ions such as potassium, sodium, lithium, cesium as well as mixtures of two or more cations are mentioned and would have advantages to be able to eliminate ammonia from the waste volume. The concentration of these silver halide solvents is preferably between 0.1 and 3.0 M and more preferably between 0.2 and 1.5 M.

As preservatives sulfites, bisulfites, metabisulfites, ascorbic acid, carbonyl-bisulfite adducts or sulfinic acid compounds are typically used. The use of sulfites, bisulfites, and metabisulfites are especially desirable. The concentration of preservatives is preferably present from zero to 0.5 M and more

The desilvered solution can then be reconstituted to return the chemical concentrations to the replenisher concentration to make up for the chemicals consumed during the bleach-fixing of the light-sensitive photographic material, or during the silver recovery treatment process, or to compensate for the dilution of the constituents caused by the carryover of solution from the previous processing stage in the process. The degree of recovery of bleach-fix solution can be measured by comparing the volume of solution that can be recovered and reused as a percentage of the original volume that was used in the process. Thus a 90% reuse recovery ratio would occur when from an original 100 L of replenisher volume 90 L would be treated and recovered to produce 100 L of regenerated fixer replenisher. The recovery reuse ratio of greater than 50% is preferred, greater than 75% is more preferred and greater than 90% is most preferred.

When an alternative process sequence is desired, separate solutions may be used for the bleaching and fixing steps. For the bleaching step, the use of a ferric complex salt of cyanide, halides, or an organic acid may be employed as the bleaching agent. The use of ferric complex salts of aminopolycarboxylic acids have been especially desirable. Examples of these complexing agents are compounds V-1 to V-20, as shown above, but are not limited only to those listed. Among these, Nos. V-1, V-2, V-3, and V-6 are preferred. If desired a combination of two or more of the aminopolycarboxylic acids may be used. Preferably the ferric complex salt may be used with a concentration between 0.01 to 1.0 M and more preferably between 0.05 and 0.5 M.

If desired, additional chelating agents may be present in the bleach solution to maintain the solubility of the ferric complex salt. Aminopolycarboxylic acids are generally used as chelating agents. The chelating agent may be the same as the organic acid in use with the ferric complex salt, or it may be a different organic acid. Examples of these complexing agents are V-1 to V-20; however, use with elements of the present photographic element is not to be construed as being limited only to those listed. Among these, V-1, V-2, V-3, and V-6 are preferred. These may be added in the free acid form or in the form of alkali metal salts, such as sodium, or potassium, or ammonium or tetraalkylammonium salts. It may be preferable to use alkali metal cations to avoid the aquatic toxicity associated with ammonium ion. The amount of the ferric complex salt added to the bleach solution is preferably 0.01 to 0.1 M and more preferably between 0.005 and 0.05 M.

Furthermore, halides (halogenating agents) are included in the bleach so that silver halide salts can form during the bleaching reactions. Halides include bromides, such as potassium bromide, sodium bromide, or ammonium bromide; or chlorides, such as potassium chloride, sodium chloride, or ammonium chloride.

The pH value of the bleach solution is preferably in the range of about 3.0 to 8.0 and most preferably in the range of about 4.0 to 6.5. In order to adjust the pH value to the above mentioned range and to maintain good pH control, a weak organic acid with a pKa between 1.5 and 7, preferably between 3 and 6, such as acetic acid, glycolic acid or malonic acid can be added in

conjunction with an alkaline agent such as aqueous ammonia. The buffering acid helps maintain consistent performance of the bleaching reaction.

In addition, mineral acids such as hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid can normally be used for the acid component and these acids can be used as a mixture with one or more salt of the weak acids previously mentioned above in order to provide a buffering effect.

Bleaching accelerators, brightening agents, defoaming agents, surfactants, fungicides, anti-corrosion agents and organic solvents, such as polyvinylpyrrolidone or methanol, as examples, may be added, if desired.

The bleach replenisher solution can be directly replenished to the bleach solution to maintain chemical concentrations and pH conditions adequate to convert the metallic silver to the ionic state as a silver halide salt. The volume of replenishment solution added per square meter of photographic light-sensitive material can be considered to be a function of the amount of silver present in the photographic light-sensitive material. It is preferred to use low volumes of replenishment solution so low silver materials are preferred. It is also preferred to use ferric complex salts organic acids with organic acid chelating agents that are biodegradable to reduce any undesirable environmental impact.

Other bleaching agents which may be used with this photographic element include compounds of polyvalent metal such as cobalt (III), chromium (VI), and copper (II), peracids, quinones, and nitro compounds. Typical peracid bleaches include the hydrogen, alkali and alkali earth salts of persulfate, peroxide, perborate, perphosphate, and percarbonate, oxygen, and the related perhalogen bleaches such as hydrogen, alkali and alkali earth salts of chlorate, bromate, iodate, perchlorate, perbromate and metaperiodate. Examples of formulations using these agents are described in *Research Disclosure*, September 1994, Item 36544, the persulfate bleaches are particularly described in *Research Disclosure*, May, 1977, Item 15704; *Research Disclosure*, August, 1981, Item 20831; DE 3,919,551 and U.S. Patent Application Serial No. 07/990,500 filed December 14, 1992. Additional hydrogen peroxide formulations are described in U.S. Patents 4,277,556; 4,328,306; 4,454,224; 4,717,649; 4,294,914; 4,737,450; and in EP 90 121624; WO 92/01972 and WO 92/07300.

Especially preferred peracid bleaches are persulfate bleaches. With sodium, potassium, or ammonium persulfate being particularly preferred. For reasons of economy and stability, sodium persulfate is most commonly used.

The bleach time may be about 10 to 240 seconds, with 40 to 90 seconds being a preferred range, and between 25 and 45 seconds being most preferred. The temperature of the bleach solution may be in the range from 20 to 50 °C with a preferred range between 25 and 40 °C and a most preferred range between 35 and 40 °C.

To minimize the volume of bleach solution that is needed to process the light-sensitive photographic material, the bleach

solution can be recovered and treated to return the chemical concentrations to the replenisher concentration to make up for any chemicals consumed during the bleaching of the light-sensitive photographic material or to compensate for the dilution of the bleach constituents by the carryover of solution from the previous processing stage in the process. The treatment to return the chemical concentrations to the replenisher concentration can be accomplished by the addition of chemicals as solid materials or as concentrated solutions of the chemicals. The degree of recovery of bleach solution can be measured by comparing the volume of solution that can be recovered and reused as a percentage of the original volume that was used in the process. Thus a 90% reuse recovery ratio would occur when from an original 100 l. of replenisher volume 90 l. would be treated and recovered to produce 100 l. of regenerated bleach replenisher. The recovery reuse ratio of greater than 50% is preferred, greater than 75% is more preferred and greater than 90% is most preferred.

Preferably, a stop bath or a stop-accelerator bath of pH less than or equal to 7.0 precedes the bleaching step and a wash bath may follow the bleach step to reduce the carryover of the bleach solution into the following fixer solution.

When a separate bleach and fixer is used, the fixer includes silver solvents, thiosulfates, thiocyanates, thioether compounds, chlorides, and thiolglycolic acid can be used. A preferred component is thiosulfate, and ammonium thiosulfate, in particular is used most commonly owing to the high solubility. If desired, other counter ions may be used in place of ammonium ion.

Alternative counterions such as potassium, sodium, lithium, cesium as well as mixtures of two or more cations are mentioned and would have advantages to be able to eliminate ammonia from the waste volume.

The concentration of these silver halide solvents is preferably between 0.1 and 3.0 M and more preferably between 0.2 and 1.5 M.

As preservatives sulfites, bisulfites, metabisulfites, ascorbic acid, carbonyl-bisulfite adducts or sulfonic acid compounds are typically used. The use of sulfites, bisulfites, and metabisulfites are especially desirable. The concentration of preservatives is preferably present from zero to 0.5 M and more preferably between 0.02 and 0.4 M.

The fixer time may be about 10 to 240 seconds, with 40 to 90 seconds being a preferred range, and between 25 and 45 seconds being most preferred. The temperature of the fixer solution may be in the range from 20 to 50 °C with a preferred range between 25 and 40 °C and a most preferred range between 35 and 40 °C.

To minimize the volume of fixer solution that is needed to process the light-sensitive photographic material, the fixer solution can be recovered and treated to remove the silver from the solution by means of electrolysis, precipitation and filtration, metallic replacement with another metal, or ion-exchange treatment with a material that will remove the silver. The desilvered solution can then be reconstituted to return the chemical concentrations to the replenisher concentration to make up for the chemicals consumed during the fixing of the light-

sensitive photographic material or during the silver recovery treatment process, or to compensate for the dilution of the constituents by the carryover of solution from the previous processing stage in the process. The treatment to return the chemical concentrations to the replenisher concentration can be accomplished by the addition of chemicals as solid materials or as concentrated solutions of the chemicals. The degree of recovery of fixer solution can be measured by comparing the volume of solution that can be recovered and reused as a percentage of the original volume that was used in the process. Thus a 90% reuse recovery ratio would occur when from an original 100 l. of replenisher volume 90 l. would be treated and recovered to produce 100 l. of regenerated fixer replenisher. The recovery reuse ratio of greater than 50% is preferred, greater than 75% is more preferred and greater than 90% is most preferred.

Preferably, following the fixer bath is a wash bath to remove chemicals from the processing solution before it is dried. Preferably the wash stage is accomplished with multiple stages to improve the efficiency of the washing action. The replenishment rate for the wash water is between 20 and 10,000 ml per square meter, preferably between 150 and 2000 ml per square meter. The solution can be recirculated with a pump and filtered with a filter material to improve the efficiency of washing and to remove any particulate matter that results in the wash tank. The temperature of the wash water is 20 to 50 °C, preferably 30 to 40 °C. To minimize the volume of water being used, the wash water that has been used to process the light-sensitive photographic material can be recovered and treated to remove chemical constituents that have washed out of the light-sensitive photographic material or that has been carried over from a previous solution by the light sensitive material. Common treatment procedures would include use of ion-exchange resins, precipitation and filtration of components, and distillation to recover purer water for reuse in the process.

To minimize the amount of water that is used to wash the light sensitive material, a solution may be employed that uses a low-replenishment rate over the range of 20 to 2000 ml per square meter, preferably between 50 and 400 ml per square meter and more preferably between 100 and 250 ml per square meter. When the replenishment rate is reduced, problems with precipitates and biogrowth may be encountered. To minimize these problems, agents can be added to control the growth of bio-organisms, for example 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one and 2-octyl-4-isothiazolin-3-one. To prevent precipitation formation preferred agents which may be added include polymers or copolymers having a pyrrolidone nucleus unit, with poly-N-vinyl-2-pyrrolidone as a preferred example. Other agents which may be added include a chelating agent from the aminocarboxylate class of chelating agents such as those that were listed previously in the description of developer constituents; a hydroxyalkylenediphosphonic acid, with 1-hydroxyethylidene-1,1-diphosphonic acid being a preferred material; an organic solubilizing agent, such as ethylene glycol; stain-reducing agents such as those mentioned as stain reducing agents for the developer

constituents; acids or bases to adjust the pH; and buffers to maintain the pH.

The stabilizer solution may also contain formaldehyde as a component to improve the stability of the dye images. However, it is preferred to minimize or eliminate the formaldehyde for safety reasons. The formaldehyde concentration can be reduced by using materials that are precursors for formaldehyde, examples include *N*-methylol-pyrazole, hexamethylenetetramine, formaldehyde-bisulfite adduct, and dimethylol urea.

To improve the efficiency of the wash it is preferred to use multiple wash stages with countercurrent replenishment of the stabilizer solution. The wash time may be about 10 to 240 seconds, with 40 to 100 seconds being a preferred range, and between 60 and 90 seconds being most preferred. The temperature of the wash stage bleach-fix solution may be in the range from 20 to 50 °C with a preferred range between 25 and 40 °C and a most preferred range between 35 and 40 °C. To further minimize the volume of water being used, the stabilizer solution that has been used to process the light-sensitive photographic material can be recovered and treated to remove chemical constituents that have washed out of the light-sensitive photographic material or that has been carried over from a previous solution by the light sensitive material. Common treatment procedures would include use of ion-exchange resins, precipitation and filtration of components, and distillation to recover pure water for reuse in the process.

B. Color Film Process

The color developer which may be used for film elements contains any of well-known aromatic primary amine color developing agents. Preferred color developing agents are aminophenol and *p*-phenylenediamine derivatives, typical, non-limiting examples of which are listed below:

- o*-aminophenol,
- p*-aminophenol,
- 5-amino-2-hydroxytoluene,
- 2-amino-3-hydroxytoluene,
- 2-hydroxy-3-amino-1,4-dimethylbenzene,
- N,N*-diethyl-*p*-phenylenediamine,
- 2-amino-5-diethylaminotoluene,
- 2-amino-5-(*N*-ethyl-*N*-laurylamino)toluene,
- 4-[*N*-ethyl-*N*-(beta-hydroxyethyl)amino]aniline,
- 2-methyl-4-(*N*-ethyl-*N*-(beta-hydroxyethyl)amino)-aniline,
- 4-amino-3-methyl-*N*-ethyl-*N*-(beta-methanesulfonamido)ethyl)aniline,
- N*-(2-amino-5-diethylaminophenylethyl)methanesulfonamide,
- N,N*-dimethyl-*p*-phenylenediamine monohydrochloride,
- 4-*N,N*-diethyl-2-methylphenylenediamine monohydrochloride,
- 4-(*N*-ethyl-*N*-2-methanesulfonaminoethyl)-2-methylphenylenediamine sesquisulfate monohydrate,
- 4-(*N*-ethyl-*N*-2-hydroxyethyl)-2-methylphenylenediamine sulfate,
- 4-amino-3-methyl-*N*-ethyl-*N*-methoxyethyl)aniline,

4-amino-3-methyl-*N*-ethyl-*N*-beta-ethoxyethyl)aniline, and
4-amino-3-methyl-*N*-ethyl-*N*-beta-butoxyethyl)aniline, and
4-*N,N*-diethyl-2'-methanesulfonaminoethyl)phenylenediamine hydrochloride.

Particularly useful primary aromatic amino color developing agents are the *p*-phenylenediamines and especially the *N,N*-dialkyl-*p*-phenylenediamines in which the alkyl groups or the aromatic nucleus can be substituted or unsubstituted.

These *p*-phenylenediamine derivatives may take salt forms, for example, sulfate, hydrochlorate, sulfite, and *p*-toluenesulfonate salts. The aromatic primary amine color developing agents are generally used in amounts of about 0.1 to 20 grams, preferably about 0.5 to 10 grams per liter of the color developer.

In addition to the primary aromatic amino color developing agent, color developing solutions typically contain a variety of other agents such as alkalis to control pH, bromides, iodides, benzyl alcohol, anti-oxidants, anti-foggants, solubilizing agents, brightening agents and so forth. The color developer may contain a preservative, for example, sulfites such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, potassium metabisulfite, and carbonyl sulfite adducts if desired. The preservative is preferably added in an amount of 0.5 to 10 grams, more preferably 1 to 5 grams per liter of the color developer.

Other useful compounds which can directly preserve the aromatic primary amine color developing agents, are for example, hydroxylamines, hydroxamic acids, hydrazines and hydrazides, phenols, hydroxyketones and aminoketones.

Photographic color developing compositions are employed in the form of aqueous alkaline working solutions having a pH of above 7, and most typically in the range of from about 9 to 13. The color developer may further contain any of known developer ingredients.

To maintain the pH within the above-defined range, various pH buffering agents are preferably used. Several non-limiting examples of the buffer agent include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium *o*-hydroxybenzoate (sodium salicylate), potassium *o*-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate), and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate), as well as other alkali metal carbonates or phosphates.

Various chelating agents may be added to the color developer as an agent for preventing precipitation of calcium and magnesium or for improving the stability of the color developer. Preferred chelating agents are organic acids, for example, aminopolycarboxylic acids, organic phosphonic acids, and phosphonocarboxylic acids. Non-limiting examples of these acids include:

nitritotriacetic acid,

diethylenetriaminediacetic acid,
 ethylenediaminetetraacetic acid,
N,N,N'-trimethylene phosphonic acid,
 ethylenediamine-*N,N',N'*-tetramethylenephosphonic acid,
 transcyclonexanediaminetetraacetic acid,
 1,2-diaminopropanetetraacetic acid,
 hydroxyethyliminodiacetic acid,
 glycol ether diamine tetraacetic acid,
 ethylenediamine-*o*-hydroxyphenylacetic acid,
 2-phosphonobutane-1,2,4-tricarboxylic acid,
 1-hydroxyethylidene-1,1-diphosphonic acid, and
N,N'-bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid.

The chelating agents may be used alone or in a mixture of two or more. The chelating agent is added to the color developer in a sufficient amount to block metal ions in the developer, for example, 0.1 to 10 grams per liter of the developer.

The color developer may contain a development promoter if desired. However, it is recommended for environmental protection, ease of preparation, and color stain prevention that the color developer is substantially free of benzyl alcohol. The term "substantially free" means that the color developer contains only up to 2 ml of benzyl alcohol or does not contain benzyl alcohol.

Useful development promoters include thioethers, *p*-phenylenediamine compounds, quaternary ammonium salts, amines, polyalkylene oxides, 1-phenyl-3-pyrazolidones and imidazoles.

The color developer may further contain an antifogant if desired. Useful antifogants are alkali metal halides such as sodium chloride, potassium bromide, potassium iodide and organic antifogants. Typical examples of the organic antifogant include nitrogenous heterocyclic compounds, for example:

benzotriazole,
 6-nitrobenzimidazole,
 5-nitrosobenzimidazole,
 5-methylbenzotriazole,
 5-nitrobenzotriazole,
 5-chlorobenzotriazole,
 2-thiazolylbenzimidazole,
 2-thiazolylmethylbenzimidazole,
 indazole,
 hydroxyazaindolizine, and
 adenine.

The color developer used herein may further contain a brightener which is typically a 4,4'-diamino-2,2'-disulfosylbene compound. It is typically used in an amount of 0 to 5 gram/liter, preferably 0.1 to 4 gram/liter.

If desired, various surface active agents, for example alkyl sulfonic acids, aryl sulfonic acids, aliphatic carboxylic acids, and aromatic carboxylic acids may be added.

The temperature at which photosensitive material is processed with the color developer is generally 20 °C to 50 °C, preferably 30 °C to 40 °C. The processing time generally ranges from 20

seconds to 5 minutes, preferably from 30 seconds to 3-1/3 minutes. The color developing bath may be divided into two or more baths if desired. In this embodiment, the color developer replenisher is preferably supplied to the first or last bath in order to shorten the developing time or reduce the replenishment amount.

With negative working silver halide, the processing step described above gives a negative image. To obtain a positive (or reversal) image, this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Desilvering may be done by separate bleach and fix steps or by a combined bleach-fix. Various combinations of these steps may also be used. Bleaching agents which may be used for film include compounds of polyvalent metal such as iron (III), cobalt (III), chromium (VI), and copper (II), peracids, quinones, and nitro compounds. Typical bleaching agents are iron (III) salts, such as ferric chloride, ferricyanides, bichromates, and organic complexes of iron (III) and cobalt (III). Ferric complexes of aminopolycarboxylic acids and persulfate are most commonly used as bleach agents with ferric complexes of aminopolycarboxylic acids being preferred. Some examples of useful ferric complexes include complexes of:

nitrioltriacetic acid,
 ethylenediaminetetraacetic acid,
 propylenediamine tetraacetic acid,
 diethylenetriamine pentaacetic acid,
o-diamine cyclonexane tetraacetic acid,
 ethylene glycol bis (aminoethyl ether) tetraacetic acid,
 diaminopropanol tetraacetic acid,
N-(2-hydroxyethyl)ethylenediamine triacetic acid,
 ethyliminodiacetic acid,
 cyclonexanediaminetetraacetic acid,
 glycol ether diamine tetraacetic acid,
 methyliminodiacetic acid,
 diaminopropanetetraacetic acid,
 ethylenediaminetetrapropionic acid,
 diaminopropanetetraacetic acid,
 iminodiacetic acid,
 ethylenediaminetetrapropionic acid,
 (2-acetamido) iminodiacetic acid,
 dihydroxyethylglycine, and
 ethylenediamine-*o*-hydroxyphenylacetic acid.

In addition, carboxylic acids such as citric acid, tartaric acid, and malic acid; persulfates; bromates; permanganates; and nitrobenzenes may be incorporated.

Preferred aminopolycarboxylic acids include 1,3-propylenediamine tetraacetic acid, methyliminodiacetic acid and ethylenediamine tetraacetic acid. The bleaching agents may be used alone or in a mixture of two or more, with useful amounts

typically being at least 0.1 M of bleaching solution, with at least 0.5 M of bleaching solution being preferred.

The redox potential of the foregoing bleaching agents is measured by the method described in *Transactions of the Faraday Society*, Volume 55, 1312-1313 (1959). Those bleaching agents having a redox potential of at least 150 mV, preferably at least 180 mV, more preferably at least 200 mV are selected for quicker bleaching. In practice, a bleaching solution containing at least 0.2 M of a bleaching agent having a redox potential of at least 150 mV ensures rapid bleaching.

In addition, water-soluble aliphatic carboxylic acids such as acetic acid, citric acid, propionic acid, hydroxyacetic acid, butyric acid, malonic acid, succinic acid and the like may be utilized in any effective amount. One or more of these are used in sufficient amount to combat the undesirable increase in blue Dmin which results from bleach induced dye formation as set forth in U.S. Patent 5,061,608. Useful amounts are typically at least 0.35 M of bleaching solution, with a least 0.7 moles being preferred and at least 0.9 moles being most preferred. Generally speaking, one uses an effective amount below the solubility limit of the acid.

These ferric aminopolycarboxylate complexes are used in the form of salts, for example as sodium, potassium, lithium, cesium or ammonium salts. These may be used alone or in a mixture of two or more. The bleaching solutions may contain other addenda known in the art to be useful in bleaching compositions, such as sequestering agents, sulfites, non-chelated salts of aminopolycarboxylic acids, bleaching accelerators, re-halogenating agents, anti-calcium agents, and/or anti-phosphate agents.

The bleaching solution is generally used at a pH of 0.45 to 9.0, more preferably 3.0 to 6.8, and most preferably 3.5 to 6.0. The bleach replenisher solution is generally at a pH of 0.2 to 8.75, more preferably 3.0 to 6.0 and is adjustable to the pH range of the bleaching solution by adding the bleach starter.

The solutions having a bleaching function are included in the processing procedures as shown below:

- 1) development → bleaching → fixing
- 2) development → bleach fixing
- 3) development → bleach fixing → fixing
- 4) development → bleaching → bleach fixing
- 5) development → bleaching → bleach fixing → fixing
- 6) development → bleaching → washing → fixing
- 7) development → washing → bleaching → fixing
- 8) development → washing → bleach fixing
- 9) development → fixing → bleach fixing
- 10) development → prebleach → bleach → optional wash → fix

The above mentioned bleach and fixing baths may have any

desired tank configuration including multiple tanks, counter current and/or co-current flow tank configurations.

The pH of the developer must be alkaline in order for proper development to occur. In contrast, the pH of the bleach must be acidic. In some processing systems there is a stop bath in between the developer and the bleach which serves to modify the alkalinity of the developer. However, many modern bleaches act as both a stop bath and a bleach for metallic silver. It is therefore necessary to use bleach replenishers which have a lower pH than the bleach tank solutions into which they are replenished. This is done in order to offset the alkaline developer solution which is carried over into the bleach solution by the photographic element. Thus, the bleaching tank solution is generally of higher pH than the bleach replenisher solution.

To start either a batch or replenished bleach tank system it is necessary to make bleach tank from a bleach replenisher solution. Bleach replenisher solutions are many times insufficient to provide desired photographic performance. When starting bleach tanks are prepared, a solution commonly known in the photographic industry as a "bleach starter" is added to the bleach replenisher solution. Water may also be added. The purpose of the bleach starter is to increase the pH of the bleach replenisher to the desired pH of the starting bleach tank solution.

Typically bleach starters are alkaline. Known bleach starters include ammonia, ammonium hydroxide, potassium hydroxide, potassium carbonate, and sodium hydroxide, aqueous ammonia, diethanolamine, monoethanolamine, imidazole, or primary or secondary amine having a hydroxyalkyl radical as an alkaline agent. U.S. Serial No. 08/183,390, filed January 19, 1994 describes the use of sodium acetate, potassium acetate and ammonium acetate as bleach starters.

The amount of the replenisher for the bleach solution is from 10 ml to 1000 ml, preferably from 30 to 800 ml per square meter. The amount of replenisher for the bleach-fix solution is from 200 to 3000 ml, and preferably from 250 ml to 1300 ml per square meter of the photographic light sensitive material. In this case the replenisher for the bleach-fix solution may be replenished as one part liquid, may be replenished separately as a bleaching composition and a fixing composition, or the replenisher for the bleach-fix solution is prepared by mixing the overflow liquids from a bleach bath and/or a fix bath.

Various bleaching accelerators can be added to the bleaching bath and the prebaths thereof. For example, there can be used the compounds having a mercapto group or a disulfide group described in U.S. Patent No. 3,893,858; German Patent No. 1,290,821; British Patent No. 1,138,842; and *Research Disclosure*, July 1978, Item 17129, the thio-urea derivatives described in U.S. Patent 3,706,561, the polyethylene oxides described in German Patent 2,748,430; and polyamine compounds.

The bleaching solution used can contain the rehalogenating agents such as bromides (for example potassium bromide, sodium bromide and ammonium bromide), and chlorides (for example

potassium chloride, sodium chloride and ammonium chloride). The concentration of the rehalogenating agent is 0.1 to 5.0 mole, preferably 0.5 to 3.0 M of the processing solution. Furthermore, ammonium nitrate is preferably used as an anti-corrosion agent to protect metal.

In processing, the bleaching solution containing the ferric complex salt of an aminopolycarboxylic acid is subjected to aeration to oxidize the formed ferric complex salt of aminopolycarboxylic acid, whereby the oxidizing agent is regenerated and the photographic properties are quite stably maintained.

In the preferred desilvering process, the photosensitive material, after bleached with the bleaching solution as mentioned above, is typically processed in a fixing or bleach-fixing solution which contains a fixing agent.

The fixing agents used herein are water-soluble solvents for silver halide such as a thiosulfate (e.g. sodium thiosulfate, ammonium thiosulfate, and potassium thiosulfate); a thiocyanate (e.g. sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate); a thioether compound (e.g. ethylenedithioglycolic acid and 3,6-dithia-1,8-octanediol); or a thiourea. These fixing agents can be used singly or in combination. Thiosulfate is preferably used.

The concentration of the fixing agent per liter is generally used in the amount of about 0.01 to 2 M of the fixing or bleach-fixing solution, although 1 to 3 M of the additional fixing agent may be used to substantially accelerate fixing if desired. The pH range of the fixing solution is preferably 3 to 10 and more preferably 5 to 9. In order to adjust the pH of the fixing solution an acid or a base may be added, such as hydrochloric acid, sulfuric acid, nitric acid, acetic acid, bicarbonate, ammonia, potassium hydroxide, sodium hydroxide, sodium carbonate or potassium carbonate.

The fixing or bleach-fixing solution may also contain a preservative such as sulfite (e.g. sodium sulfite, potassium sulfite, and ammonium sulfite), a bisulfite (e.g. ammonium bisulfite, sodium bisulfite, and potassium bisulfite), and a metabisulfite (e.g. potassium metabisulfite, sodium metabisulfite, and ammonium metabisulfite), and bisulfite adducts of hydroxylamine, hydrazine and aldehyde compounds (e.g. acetaldehyde sodium bisulfite). The content of these compounds is about 0 to 0.50 M, and more preferably 0.02 to 0.40 M as an amount of sulfite ion. Ascorbic acid, a carbonyl bisulfite acid adduct, or a carbonyl compound may also be used as a preservative.

The bleach-fixing solution may contain any well-known bleaching agents as previously mentioned. Preferred are ferric aminopolycarboxylate complexes. The bleach-fixing solution generally contains 0.01 to 0.5 mole, preferably 0.015 to 0.3 mole, more preferably 0.02 to 0.2 mole of the bleaching agent per liter of the solution.

Further, from the viewpoint of accelerating of fixing, preferably used are above mentioned ammonium thiocyanate (ammonium rhodanate), thiourea and thioether (for example, 3,6-dithia-1,8-octanediol) in combination with thiosulfates. The amount of these

compounds used in combination with thiosulfate is 0.01 to 1 mole, preferably 0.1 to 0.5 M of the processing solution having fixing ability. On some occasions, the use of 1 to 3 mole can increase the fixing-acceleration to a very large extent.

The amount of the replenisher for the fix solution is from 5 to 300 ml, and preferably from 5 to 120 ml per square foot of the photographic light-sensitive material.

The processing composition is fundamentally composed of the foregoing color development step and the subsequent desilvering step. It is preferred to employ a wash step and/or a stabilization step after the desilvering step.

Wash water used for the wash step can contain various kinds of surface active agents for prevention of the occurrence of water drop unevenness when the color photographic materials are dried.

The surface active agents include polyethylene glycol type nonionic surface active agents, polyhydric alcohol type nonionic surface active agents, alkybenzenesulfonate type anionic surface active agents, higher alcohol surfuric acid ester type anionic surface active agents, alkylphthalenesulfonate type anionic surface active agents, amine salt type cationic surface active agents, quaternary ammonium salt type cationic surface active agents, and amino acid type amphoteric surface active agents.

However, since ionic surface active agents combine, as the case may be, with various ions entering with processing to form insoluble materials, a nonionic surface active agent is preferred and an alkylphenolethylene oxide addition product is particularly preferable, alkylphenol, octylphenol, nonylphenol, dodecylphenol and di-nonylphenol are particularly preferred. The addition of ethyleneoxide in the range of 8 to 14 moles is preferable. Furthermore, it is also preferred to use a silicone series surface active agent having a high defoaming effect.

Also, wash water can contain various anti-bacterial agents or antifungal agents for preventing the growth of fungi in the photographic light-sensitive materials after processing.

These antibacterial agents and antifungal agents include thiazolylbenzimidazoles, isothiazolones, and chlorophenols such as trichlorophenol, bromophenols, organochin or organozinc compounds, thioether or isothioetheric acid compounds, acid amides, diazine or triazines, thioureas, benzotriazolealkylguanidines, quaternary ammonium salts such as benzammonium chloride, antibiotics such as penicillin and the antifungal agents described in *Journal of Antibacterial and Antifungal Agents*, V. 11, No. 5, 207-223 (1983).

The relationship of the number of wash tanks and the amount of wash water in a multistage counter-current system can be obtained by the method described in *Journal of the Society of Motion Picture and Television Engineers*, V. 64, 248-253 (May 1955). In accordance with the multistage counter-current system described in the above publication, the amount of wash water can be greatly reduced.

The stabilization solution which is used for the stabilization step is one for stabilizing dye images. For example, a liquid containing an organic acid and a buffer of pH from 3 to 6 or a liquid containing an aldehyde (e.g. formaldehyde

and glutaraldehyde) can be used. Where the stabilization solution is used at the final step it is used in the pH ranging from 4 to 9, preferably from 6 to 8. Where the stabilizing solution is used at the final step, the processing temperature is preferably 30 °C to 45 °C; the processing time is preferably 10 seconds to 2 minutes.

The stabilization solution can contain all the compounds which can be added to wash water and also contain, if necessary, ammonium compounds such as ammonium chloride, ammonium sulfite, etc.; compounds of a metal such as Bi, Al, etc.; optical whitening agents; N-methylol compounds as described in U.S. Patent 4,859,574; various kinds of stabilizers, hardening agents, and the alkanolamines described in U.S. Patent 4,786,583, and those described in U.S. Patent 5,217,852, and European Patent Application No. 551,757A1.

For the purpose of preventing scums there are preferably incorporated therein sorbitan esters of fatty acids substituted with ethylene oxide as described in U.S. Patent 4,839,262, and polyoxyethylene compounds described in U.S. Patent 4,059,446, and *Research Disclosure*, Vol. 191, 19104 (1980).

In the wash step or the stabilization step, a multistage countercurrent system is preferably used and the number of stages is preferably from 2 to 4. The amount of replenisher is from 1 to 50 times, preferably from 2 to 30 times, and more preferably from 2 to 15 times the amount carried from the pre-bath per unit area.

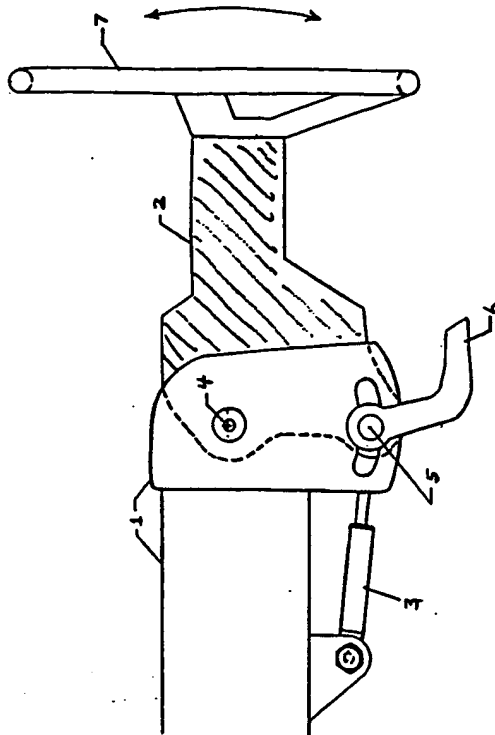
The water for the wash step or the stabilization step may be city water, but deionized water having calcium and magnesium concentrations of less than 5 mg/liter with ion exchange resins and water sterilized with a halogen or an ultraviolet sterilizing lamp are preferably used. City water may be used to replace evaporated water, but it is preferred to use deionized water or sterilized water.

Disclosed Anonymously
37038

37039

Impact Proof Infinite Tilt Steering Column With Anti-Slam Feature

The steering column lower support 1 is rigidly fixed to the automobile. The steering wheel 7 is attached to the tilt head 2 and allowed to rotate up and down around pivot point 4. The tilt head is spring loaded to lift the tilt head and wheel up from an position. The tilt head 2 is secured to the lower support around point 3 by means of a frictional clamping device that can be locked and released by the lever 6. The damper 3 is connected between the lower support 1 and the tilt head 2. The damper controls the velocity of the tilt head and prevents the tilt head and wheel from slamming into its upper most position. In addition, the damper resists the high velocity and short duration impact force the column must withstand during a collision. The damper helps take this load that the friction lock can not hold on its own.



Disclosed Anonymously
37039

In the liquid propellant intelligent air bag system an ambient passenger compartment temperature sensor and a liquid propellant temperature sensor are utilized together with an occupant position and occupant size sensor to control the heating and cooling of the liquid propellant to achieve the desired pressure in the air bag upon deployment.

Controller 1, based on the information provided by the occupant position sensor 4, the occupant weight sensor 6, the passenger compartment ambient temperature condition sensor 8, and the propellant temperature sensing means 12, determines the amount of heating or cooling required for the liquid propellant. Controller 1 then activates heater 14 to provide heat to the liquid propellant or activates cooler 16 to cool the liquid propellant as required.

